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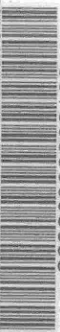
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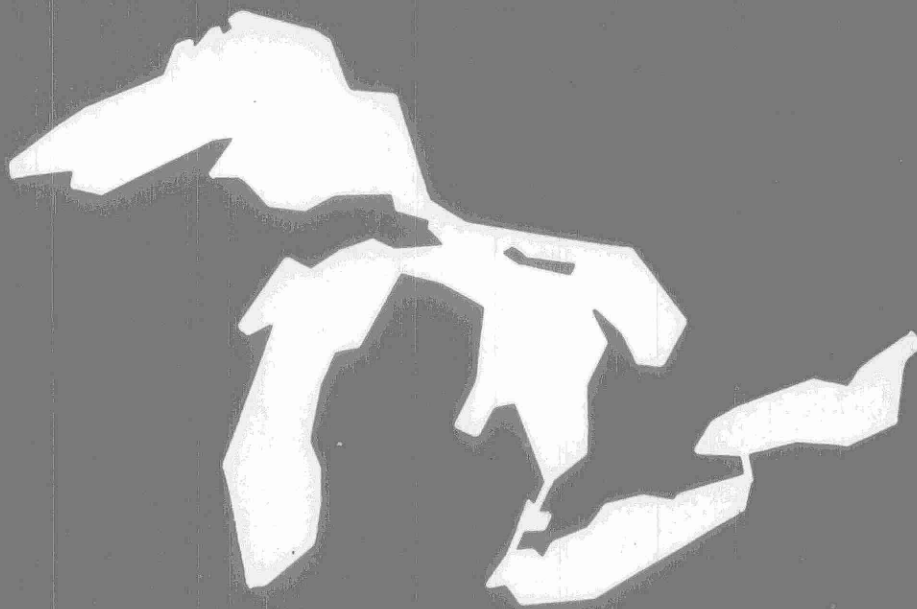
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Recycling of Incinerator Ash Research Report No. 19



**Research Program for the Abatement of Municipal Pollution
under Provisions of the Canada-Ontario Agreement
on Great Lakes Water Quality**

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RECYCLING OF INCINERATOR ASH

by

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RESEARCH PROGRAM FOR THE ABATEMENT
OF MUNICIPAL POLLUTION WITHIN THE
PROVISIONS OF THE CANADA-ONTARIO
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ABSTRACT

A preliminary study on the recovery of valuable components of incinerated sewage sludge ash was completed. Methods of solubilizing the phosphorus, iron, aluminum and heavy metal content of the ash were investigated, and standard recovery and separation procedures were attempted.

The recovery of iron and aluminum from the ash was found to be economically unattractive; however, the recovery of phosphorus in the form of phosphoric acid was possible. A large percentage of heavy metals was found to be tied up in refractory oxides, formed during incineration. These refractories are chemically highly resistant, preventing solubilization by most solvents. The alteration of incineration conditions may remove this problem.

A preliminary cost estimate for a pilot plant treating 300 lb/hr ash is presented, based on a flowsheet for phosphoric acid recovery.

RÉSUMÉ

On a terminé une étude préliminaire de la récupération des constituants de valeur des cendres obtenues de l'incinération de boues résiduelles. On a fait des recherches sur les méthodes de solubilisation du phosphore, du fer, de l'aluminium et des métaux lourds contenus dans ces cendres, et on a tenté d'instituer des méthodes normales de récupération et de séparation.

La récupération du fer et de l'aluminium contenus dans les cendres ne s'est pas révélée économiquement attrayante; toutefois, la récupération du phosphore sous forme d'acide phosphorique est possible. On a découvert qu'un gros pourcentage des métaux lourds faisaient partie d'oxydes difficilement séparables formés par l'incinération. Ce sont des composés très résistants du point de vue chimique, ce qui empêche leur solubilisation dans la plupart des solvants. La modification des conditions d'incinération peut éliminer ce problème.

On présente une estimation préliminaire de coûts pour une unité pilote traitant 300 lb/heure de cendres, basée sur le schéma de la récupération de l'acide phosphorique.

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CONCLUSIONS AND RECOMMENDATIONS

Despite the preliminary nature of this study, several important conclusions were reached.

The data indicate that heavy metals leach out of the ash even with neutral distilled water. On prolonged contact (2-3 hours) approximately 1 mg/l chromium has been measured in the water. Since natural waters are often acidic, considerably higher leaching rates might be expected. The potential of environmental contamination by heavy metals warrants a closer examination of ash disposal methods, and may provide a non-economic incentive to ash recycling.

Aluminum and iron sulphates are chemicals added during sewage treatment. Their recovery would be of great benefit and convenience to sewage treatment plant operations. This study found this approach to be uneconomical, as was predicted. Iron was present at relatively low levels of about 4-5%. Magnetic iron oxide was present but iron recovery from this form is impractical, since the cost would be several times higher than the commercial cost of ferrous sulphate.

Similarly, aluminum was present in the form of a refractory oxide that is not responsive to any inexpensive chemical treatment. While the recovery of these flocculants may be possible, recovery must be made before the formation of intractable oxides by incineration.

The analyses of the ash revealed that the variable composition of the sewage was exaggerated in the incinerated ash. The ash was highly inhomogeneous, especially in the heavy metals. The composition changed very rapidly, on a time scale of a few minutes; however, the overall characteristics of the ash remained fairly constant.

Approximately 50% of the ash was in the chemically inert form of silicates and alumina. This study found that a large proportion of all heavy metals, especially zinc and chromium, was physically or chemically bound by these refractories, which are not available through acid digestion. When these compounds were released by alkaline fusion, analyses of the ten major ash components gave a mass balance of 98%.

The presence of 20-50% strongly bound heavy metals in the ash suggests that perhaps the simplest approach to safe ash disposal may be in

the formation of refractories from all ash components. By the addition of some fluxing agents, or by altering the incinerator conditions, it may be possible, and beneficial, to produce a glasslike "ash" that will contain much lower quantities of leachable heavy metals than the present ash.

Phosphorus represents the highest economic value in the ash. It is present to the extent of 14-18% expressed as phosphoric acid. Since practically all of Canada's phosphorus is imported as phosphate rock, the recovery of the phosphate seems most advantageous. Recently the price of phosphate rock was increased considerably on the international market, and the phosphate value of the ash is currently some \$46.00 per ton.

Phosphorus is readily solubilized by either phosphoric or 60% sulphuric acids. The use of H_2SO_4 permits the removal of the inert calcium sulphate and iron oxides. The remaining heavy metals must be removed by ion exchange if metal free phosphoric acid is to be recovered by sulphuric acid distillation. Another alternative would remove the phosphoric acid by liquid-liquid extraction followed by solvent recovery.

The metal content of the leaching liquor may be concentrated by ion exchange, and recovered by sulphide precipitation. The extremely low dissociation product of heavy metal sulphides provides perhaps the most efficient removal of these metals from water.

Chromium or zinc may be concentrated by special procedures where the total quantity present in the ash warrants it.

In summary, only phosphate recovery seems economically warranted. However, the study of recovery processes should be expanded, since there are indications that the ash in its present form may contribute to the heavy metal loading of groundwater.

1. INTRODUCTION

The conventional activated sludge treatment of municipal sewage results in a very large volume of sludge containing 2 to 10% solids. The disposal of these wet solids is complicated by their high organic content and the air pollution problems related to their incineration. In large sewage treatment plants, with capacities in the order of 100 MGD, the sludge is incinerated to reduce the volume of solids handled.

Sewage sludge incineration normally takes place in a flame or in a multiple hearth furnace after dewatering by centrifuges to 10 - 25% solid content. The resultant ash is free of organics, and it is considered suitable for landfill.

Recent investigation of the composition of sewage sludge has indicated that very high levels of toxic heavy metals may be concentrated in the biomass of the sludge. These heavy metals, with the exception of the highly volatile mercury, are doubtless further concentrated in the incinerated ash. Although these ashes are considered inert, and safe for land disposal, some heavy metal compounds may be leachable under favourable circumstances, resulting in environmental damage.

Cambrian Processes Limited has investigated the removal of phosphates and heavy metals from incinerated sewage sludge ash, and the recovery of components of economical value. The basic aims of the study were twofold:

1. To produce a solid free of leachable toxic components from the ash.
2. To extract compounds of economic value.

The scope of the project included the following main areas:

1. Literature review.
2. Examination of:
 - a. ash composition,
 - b. solubility of ash components, and
 - c. separation techniques
3. Economic evaluation of promising separation methods and estimation of the equipment requirements for a pilot plant to utilize the most feasible flowsheet.

The following report presents the results of this preliminary study on the feasibility of iron, aluminium, heavy metals and phosphorus recovery from incinerated sewage sludge ash.

2. LITERATURE REVIEW

Conventional wastewater treatment plants decrease the total solids content of the water. The bulk of the organic components of water are removed as carbon dioxide or methane by microbial action, while a large portion of the remaining organic and inorganic solids is recovered in the form of sewage sludge.

Municipal treatment plants produce very large volumes of sludge. The Ashbridge's Bay treatment plant in Toronto treats 180 MGD of sewage, and recovers some 1.8 million pounds of sludge daily. The volume of sludge produced in Ontario sewage treatment facilities is expected to rise rapidly in the near future, as phosphate removal processes will be installed at all major plants (Ontario Ministry of Environment, 1972).

The disposal of sewage sludge has been a constant problem to the treatment plants. In rural communities sludge has been used as fertilizer. Recent advances in the analysis of heavy metals have revealed potential problems with this disposal method. Land disposal of sludges has been opposed (LeRiche, 1968) by researchers in the U.K. and in Ontario on the basis of their high metal contents. Nickel, chromium, copper and zinc levels of up to 1000 times the normal background levels have been observed in sludges dispersed in landfill areas.

The incineration of sewage sludge has become an increasingly acceptable method of reducing both the volume and chemical activity of the solid wastes from sewage treatment facilities. Many large treatment facilities in North America have installed sludge incinerators. Incinerator ash contains some 50% of the total solids in sludge on a dry basis, or less than 8% on a wet basis. In addition to this obvious gain in volume, the ash is simpler to handle and seems chemically inert (Warfe, 1974).

The search of the literature revealed a marked interest in recycling materials of economic importance; however, no references to recycling incinerated sewage sludge ash were found.

Conventional methods of phosphoric acid production (Ullmann, 1969) usually consist of hydrolysis of the phosphoric acid from calcium phosphate by sulphuric acid, followed by filtration of calcium sulphate and vacuum

distillation of excess sulphuric acid. Baniel et al (1959) have discussed a similar scheme using HCL, followed by solvent extraction of the phosphoric acid. Since the ash contains a high percentage of phosphates, which will increase with further phosphate removal treatments, phosphoric acid manufacturing methods may be applicable to sewage sludge ash recycling.

Conventional mineral processing for the metal content of ash did not seem practical, since all mineral separation systems rely on the surface properties of microcrystalline solids and this type of order is not present in ash components. The standard methods of analytical chemistry were reviewed and attempted in the later experiments.

In summary, the literature contains several useful references on the potential composition of the ash, however, the majority of the applicable literature deals with sludge disposal and recycling, without direct reference to ash leaching or recovery.

3. EXPERIMENTAL SECTION

The experimental work was concentrated in three separate areas:

- 1) Determination of ash composition and its variation.
- 2) Solubilization of ash components.
- 3) Separation techniques.

The determination of ash composition was vital for assessment of the economic potential of the recovery processes, as well as serving as the basis for all further analytical work.

Special emphasis was placed on the solubilization of ash components, since no work dealing directly with this problem was found in the published literature.

The separation techniques for soluble components were not examined in depth since there is considerable industrial expertise available for these processes and in general their theoretical basis is well understood. Only a few experiments were carried out to test feasibility, without attempting to obtain a quantitative optimization of reaction conditions. While this detailed work must be done before process designs for operating plants can be obtained, it was felt that more valuable information could be gained within the scope of this project by concentrating on the fundamental problem of solubilization of ash components.

3.1 Ash Analysis

3.1.1 Source of samples

Three composite ash samples were obtained from the Ashbridge's Bay Sewage Treatment Plant, at approximately three month intervals during 1973. The samples, 5 - 10 kg each, were obtained directly from the outlet end of the incinerator, while the ash was still warm.

3.1.2 Description of the ash

The Ashbridge's Bay sewage treatment plant is the major treatment facility in Metropolitan Toronto. The plant has a design capacity of 180 MGD. The multiple hearth incinerator normally handles 38 tons of sludge per hour, containing 15% solids. Some 50% of the total solids are recovered as ash amounting to some 70 tons/day. Currently the plant

is operating at 20 - 30% above the design capacity. Phosphate removal had not yet been initiated at the time of this study.

The ash emerges from the incinerator as brown irregular agglomerates. The grain size varies from sub-200 US mesh up to 1/2 inch, with the bulk of the solids in the 1/4 inch to 1/8 inch range. Larger sizes are primarily the result of localized fusion. The agglomeration of particles by fusion does not seem to be a problem in Ashbridge's Bay although in Hamilton it has been known to cause operational difficulties.

The brown colour of the ash may be attributed to a magnetic iron oxide surface covering. On grinding 5 - 10 kg samples, the ash assumed a light tan colour, indicating that the iron is preferentially deposited, or oxidized on or near the particle surfaces. The ash consisted of the following main components:

- a) silicates - from unsettlable dust particles.
- b) phosphates - from the phosphorus content of sewage.
- c) sulphates - from domestic sewage and industrial wastes.
- d) refractory metal oxides - primarily oxidized during incineration.

Metals such as zinc and chromium originate with the domestic and industrial sewage, while a sizeable portion of the iron and aluminum content of the water is introduced during the sewage treatment process.

The amount of aluminum, iron and phosphorus present in the ash is considerably increased by the introduction of phosphate removal processes. It is expected that all Ontario sewage treatment facilities on the Great Lakes System with capacities over 1 MGD will be removing phosphates to less than 1 mg/l as P by December 1975.

3.1.3 Analytical methods

The metal content of the ash was analysed by atomic absorption spectrophotometry, after acid digestion in an oxidizing medium. Perchloric acid or aqua regia (mixture of concentrated nitric and hydrochloric acids) was used for digestion. Phosphates were analysed spectrophotometrically, while sulphates were gravimetrically determined after acid digestion. Generally the methods set out in the Standard Methods for the Examination

of Water and Waste Water, 13th edition, were used. Several grab samples of approximately 10 grams were initially obtained from the composite samples. These were ground to sub-200 US mesh and homogenized before weighing out duplicate or triplicate 1 gram aliquots. The samples were digested with 25 ml acid, and after digestion they were made up to 50 ml with the same acid solution. Blanks of the acid were identically prepared.

The volumetric samples were filtered through acid washed fibreglass filter papers, and after appropriate dilution and preparation, analysed for metals and phosphorus. All data are reported as μg of component ion per gram of dry ash.

3.1.4 Analytical results

The background analyses using aqua regia are presented in Table 1. Table 2 contains the analytical data using perchloric acid as the digesting agent. The data for Series 2 were obtained from grab samples while the results of Series 3 were obtained after milling a 5 kg composite sample to 200 mesh (approximately 100 micron maximum particle size) and homogenizing the whole sample. Results for Series 1, using perchloric acid, were obtained on individual grab samples. A complete listing of all analytical measurements is present in the Appendix.

3.1.5 Discussion

The purpose of the ash analyses was to establish an analytical basis for the project. The estimated economic potential of the ash and the efficiency of the recovery processes are based on these background analyses.

While a complete statistical evaluation of ash composition would require a study on its own, an indication of the average ash composition and its variation was obtained. It was found that the ash composition varied widely on a very short time scale; as shown in Table 2, portions of a sample taken within a two minute interval showed considerable discontinuity.

Each of the three sample batches had an individual element distribution, despite similar chemical characteristics. In each sample, the largest constituents were silica and calcium. While aluminum was not

TABLE 1

ASH ANALYSES

using aqua regia for digestionSERIES 2SERIES 3

ELEMENTS	AVERAGE	STANDARD	AVERAGE	STANDARD
	$\mu\text{g/g}$ SAMPLE	DEVIATION $\mu\text{g/g}$ SAMPLE	$\mu\text{g/g}$ SAMPLE	DEVIATION $\mu\text{g/g}$ SAMPLE
Ca	87,300	4,400	103,700	2,500
Cr	3,500	550	4,180	412
Cu	1,950	150	2,200	41
Fe	31,600	980	38,800	342
Mg	12,400	627	12,000	134
Ni	539	48	304	10
Pb	1,760	497	1,640	63
Zn	4,110	777	5,920	718
P	52,700	982	56,300	1,460

TABLE 2

ASH ANALYSES

SERIES 1

PERCHLORIC ACID DIGESTION, OF INDIVIDUAL GRAB SAMPLES

<u>ELEMENTS</u>	<u>SAMPLE 1</u> <u>µg/g ASH</u>	<u>SAMPLE 2</u> <u>µg/g ASH</u>	<u>SAMPLE 3</u> <u>µg/g ASH</u>
Ca	110,400	114,000	112,200
Cr	5,000	2,900	6,500
Cu	2,700	1,890	3,100
Fe	38,700	35,000	32,700
Mg	15,400	10,300	16,200
Ni	1,350	1,120	1,400
Pb	1,300	1,540	1,000
Zn	9,900	8,500	9,100
P	45,100	36,200	42,100

available by standard digestion techniques, the samples contained 8 - 10% aluminum, present as alumina. Phosphorus, iron, and magnesium were the other main components present in concentrations above 1%. Zinc, copper and chromium were present in various quantities approaching values found in low grade ores. Lesser quantities of nickel and lead were found. However, even these quantities were much higher than that normally found in soils, and thus they could have an adverse ecological impact.

As expected, mercury was not present in measurable quantities, since it is removed during incineration as mercury vapor.

To ensure a uniform analytical base, all of sample 3 was ground in a ball mill to sub-200 US mesh size. This procedure yielded the most reliable analytical results, as shown by the low standard deviations in Series 3 (Table 1).

The variation of individual elemental concentrations is shown in Table 3. As expected, the least variation was encountered in the main ash components: calcium, iron and phosphorus. The major changes in nickel, chromium, lead and zinc concentrations were probably due to variations in industrial activity.

3.2 Solubility Studies

The separation of chemical components from a solid matrix may be based on physical, chemical or surface chemical properties. Physical separation techniques may use specific gravity differentials or electromagnetic properties as the driving force. Surface chemical properties are widely used for separating ore components that are present as small, discrete, homogeneous crystals. These techniques, however, are of little value in complex systems such as sewage ash.

In the ash, the different components are often chemically and crystallographically interconnected, and separations are only possible at the molecular or atomic level. Thus the standard mining procedure of fine grinding and froth flotation of individual mineral particles will not yield any "elemental" fractionation. Chemical methods must be used to separate the different components. Chemical separation of solids, with a few exceptions, must be carried out, at least partially,

TABLE 3
VARIATION OF ANALYTICAL DATA

<u>ELEMENTS</u>	<u>HIGH VALUE</u> <u>μg/g</u>	<u>LOW VALUE</u> <u>μg/g</u>	<u>WEIGHTED AVERAGE</u> <u>μg/g</u>	<u>% VARIATION</u> <u>FROM AVERAGE</u>
Ca	112,000	87,200	102,000	14.5
Cr	6,500	2,790	4,090	58.9
Cu	3,100	1,770	2,180	42.2
Fe	39,300	29,900	35,200	15.1
Mg	16,200	9,950	12,400	30.7
Ni	1,400	252	600	133
Pb	2,600	1,000	1,590	63.5
Zn	9,900	3,090	6,020	64.5
P	59,200	36,200	50,900	28.9

in the liquid phase. The separation may proceed by:

- 1) differential dissolution, or leaching of the component of interest;
- 2) complete dissolution of the matrix, leaving behind the valuable components;
- 3) differential crystallization of the valuable components from solution (or melt); and,
- 4) liquid-liquid or liquid-solid partition of components prior to separation by crystallization.

The partial or complete solubilization of ash components is, therefore, the most important step in separation and recovery of economically important ash components. Accordingly the majority of experimental work in this project was concentrated on the determination of ash solubility in different acids, bases and salts.

3.2.1 Experimental method

Solubility experiments were performed under similar conditions for each solvent. Approximately one gram samples of ash, accurately weighed, were boiled under reflux with 25 grams solvent for two hours. The sample was then filtered through fibreglass or asbestos paper, and the remaining solids were discarded. The supernatant was made up to 50 ml with the solvent, and after appropriate preparation and dilution, analysed.

The analytical results were reported as $\mu\text{g/g}$ ash solubilized, and also as % of aqua regia soluble component in the same ash batch.

Results were reported for calcium, chromium, copper, iron, lead, magnesium, nickel, phosphorus, and zinc. Aluminum was determined on the most pertinent (12) samples. Mercury and cadmium analyses were impractical, as in all cases the levels were below the analytical error on the background ash analyses.

3.2.2 Solubility in water

It was hypothesized that the incinerated ash was not completely inert. At the present, the ash is disposed of in landfill, and in Ashbridge's Bay it is dumped in or near Lake Ontario. To test the hypothesis that some of the metals present in the ash are indeed leachable

by water, the water-solubility of the ash was tested, using pH 7 distilled deionized water. The ash was left in contact with water for 24 hours on a water bath, then analysed for metals. The analytical results are given in Table 4 below.

TABLE 4. WATER SOLUBILITY OF ASH.

Component	Average Solubility ug/g ash	Concentration in Water mg/l	% of Component Soluble in Water
Ca	3230.0	135.0	3.12
Cr	18.0	0.75	0.43
Cu	0.6	0.025	0.02
Fe	0.2	0.008	--
Mg	521.0	21.7	4.34
Ni	--	--	--
Pb	--	--	--
Zn	3.0	0.12	--
P	25.2	1.05	0.04

The results indicated that potentially high concentrations of chromium may be present in water percolating through the ash. Since the quantity of water in contact with the ash after land disposal will be much higher than 25 to 1 w/w, in the long run a higher proportion of the heavy metal content of the ash may be leached out. Similarly, the non-neutral pH of natural waters may accelerate this process. While the results show no drastically high contamination, the leaching of the metal content of ashes by groundwater should be investigated.

3.2.3 Solubility in mineral acids

The solubility of the ash in concentrated mineral acids was investigated, since these are potentially excellent solvents for non-refractory oxides and some may, in addition, hydrolyze phosphates to phosphoric acid. Sulphuric, nitric, hydrochloric and phosphoric acid were investigated. The solubility data, expressed as percent of background analysis by aqua regia, are presented in Table 5. All data are compensated for the presence of metals in the reagents by "blank"

determinations identically treated.

TABLE 5. SOLUBILITY OF ASH IN CONCENTRATED MINERAL ACIDS

	Ca	Cr	Cu	Fe	Mg	Ni	Pb	Zn	P
	%*	%	%	%	%	%	%	%	%
H ₂ SO ₄	92.5	75.8	120.9	0.7	57	94.1	17.2	178.3	92
HNO ₃	45.4	37.4	49.5	40.7	47.2	28.2	49.5	32.7	66.6
HCL	86.2	109.2	94.2	102.1	93.2	102.3	96.1	107.4	103.4
H ₃ PO ₄	98.1	97.4	48.7	97.7	98.0	96.1	88.2	37.8	--

* All data based on aqua regia solubility = 100%

It was immediately obvious that some metallic compounds were not completely digestible with aqua regia, while reacting further with other mineral acids. While the standard deviation of the analyses is better than 2 % and the deviation between samples is no worse than 5%, solubilities as high as 178% Zn were obtained using sulphuric acid as solvent. (All data points represent at least duplicates; usually 4 parallel samples were run). The results, in summary, indicate that sulphuric acid is an efficient solvent for all components except iron and lead. Magnesium was soluble to the extent of 57%. Copper and especially zinc were more available to sulphuric acid than to aqua regia.

Nitric acid was found to be a poor solvent for all components. It is inefficient in solubilization as well as fractionation, since all components are dissolved to the extent of 30 - 50 %.

Hydrochloric acid was a highly efficient general solvent, with no special affinity for any of the elements analysed.

Phosphoric acid was also found to be a remarkably good solvent for all elements except copper (49%) and zinc (37.8%). Phosphorus was very difficult to analyse due to solvent effects.

On the basis of the above data, both the H₂SO₄ and the H₃PO₄ systems were further investigated.

3.2.4 Solubility in miscellaneous solvents

Ash solubility in weak acids, highly ionic salts and aqueous alkalis was also investigated. Eight systems were tried: acetic acid and

citric acid as weak acids; EDTA and a household detergent as metal sequestering agents; sodium persulphate, hydrogen peroxide and sulphuric-nitric acid mixture as oxidizing agents; and, aqueous sodium hydroxide as a strong base. The solubility data, expressed as percentages based on aqua regia analyses, are summarized in Table 6.

Neither acetic, nor citric acid were efficient solvents, as all components were only weakly soluble, without any fractionation.

Both EDTA and the household detergent "Tide" (Procter & Gamble Ltd.) had very high recovery efficiencies for nickel, with the detergent showing an unexpectedly high specific affinity. Due to its cost and non-specificity EDTA may be discarded as a viable "solvent", however, in systems where nickel values are very high, detergents may justify some research interest.

Hydrogen peroxide, sodium persulphate and sulphuric acid-nitric acid mixtures were used in order to find a more comprehensive data base than that given by aqua regia digestion. However, none of these systems were suitable for analytical purposes.

Hydrogen peroxide gave very high chromium and zinc values, but other recoveries were poor, and no fractionation of practical importance took place.

Sodium persulphate gave excellent recovery efficiencies, with good calcium and lead rejection. This system warranted further investigation, and therefore three series of experiments, reported in section 3.2.7 were performed.

The sulphuric acid-nitric acid system also showed high recovery efficiencies for zinc, copper and chromium, and since it is often reported as an analytical digestion medium, the whole concentration range was cursorily examined. (Section 3.2.6)

Sodium hydroxide shows promise as an excellent fractionating solvent. It dissolved the majority of phosphorus and zinc while leaving all, except traces of the other components, in the solid phase.

3.2.5 Solubility in sulphuric acid solutions

The solubility of ash components was examined with sulphuric acid solutions of different concentrations (Table 7). The acid concentration had

TABLE 6

ASH SOLUBILITY IN MISCELLANEOUS SOLVENT SYSTEMS

<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
Acetic Acid 100%	4.3	8.2	13.2	4.0	21.9	5.7	18.6	1.9	0.1
50% Aqueous Citric Acid	81.8	17.9	27.2	46.5	62.4	11.3	25.1	32.0	52.7
1% Aqueous EDTA	54.4	12.6	42.5	25.0	55.4	100.0	37.2	16.0	51.2
30% Aqueous Detergent	--	22.6	8.7	0.8	2.2	97.8	15.3	2.1	Not determined
9% H ₂ O ₂ /70% H ₂ SO ₄	55.8	194.0*	20.3	30.3	81.5	20.4	15.9	208.0*	81.7
30% Aqueous Na ₂ S ₂ O ₇	13.9	127.3*	111.6	90.3	119.3	105.2	5.9	168.3	96.2
75% H ₂ SO ₄ /25% HNO ₃	47.7	169.8	120.1	48.4	72.0	16.1	13.6	196.0	69.0
40% Aqueous NaOH	--	7.3	0.9	0.5	0.02	2.8	4.7	51.2	63.7

All solubilities expressed as percentages, where aqua regia solubility is 100%

TABLE 7

ASH SOLUBILITY IN AQUEOUS SULPHURIC ACID SOLUTIONS

<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
H ₂ SO ₄ 10%	26.4	59.1	83.7	124.0	96.6	51.8	9.0	58.2	64.2
H ₂ SO ₄ 30%	6.0	182.8	128.0	111.5	80.5	119.7	6.3	195.4	87.9
H ₂ SO ₄ 40%	1.5	148.2	117.5	115.0	110.6	145.2	6.3	180.4	89.8
H ₂ SO ₄ 60%	0.6	148.5	107.8	7.0	89.9	154.1	6.2	193.4	83.1
H ₂ SO ₄ 70%	7.7	165.9	120.5	2.7	62.8	163.3	9.2	184.4	83.6
H ₂ SO ₄ 80%	57.9	138.6	115.4	0.9	58.0	179.8	16.8	193.3	84.6
H ₂ SO ₄ 100%	92.5	75.8	120.9	0.7	57.1	94.1	17.2	178.3	92.4

All data expressed in % of aqua regia solubility

a marked effect on all components except lead, where the solubility was nearly constant at a low (10%) level throughout the composition range of 1 to 100 % H_2SO_4 .

As expected, calcium exhibited almost no solubility in the 40-60% acid concentration range, with markedly higher solubility at both higher and lower concentrations.

Magnesium showed an opposite effect: a very sharply defined solubility maximum was observed between 40 and 50% H_2SO_4 (Figure 1).

Iron also had a highly characteristic response to acid concentration: while the solubility was almost constant in the ranges of 1 to 40% acid and 60 to 100% acid, there was a tenfold decrease in solubility between 50 and 60% H_2SO_4 .

Nickel solubility increased rapidly with increasing acid concentration throughout the range of 1 to 100% H_2SO_4 (Figure 2).

Copper and phosphorus both showed increased solubility with increased concentration in the lower concentration ranges, which levelled off to near constant values above 50% H_2SO_4 (Figure 3).

Both of the remaining metals that were examined had a broad solubility maximum in the 30 - 80% H_2SO_4 range. However, there was considerable scatter in the data. Both zinc and chromium showed a marked decrease in solubility at both the 1 and 100% H_2SO_4 concentrations (Figure 4).

On the basis of these solubility data a very useful fractionation of the ash components seems possible: by choosing a concentration in the 50 - 60% range, the bulk of all components except lead, calcium and iron may be dissolved. Calcium and lead remain as inert sulphates, while the iron is unaltered from its oxide form, rendering the undissolved solid fraction inert and suitable for disposal.

The further separation of metals may be effected by classical chemical methods.

3.2.6 Ash solubility in nitric acid - sulphuric acid mixtures

The mixture of sulphuric and nitric acids is often used as the digestion medium in water analyses, since the combination is a highly ionic strong acid, as well as an oxidizing agent. A series of mixtures were investigated to determine their efficiency for dissolving different

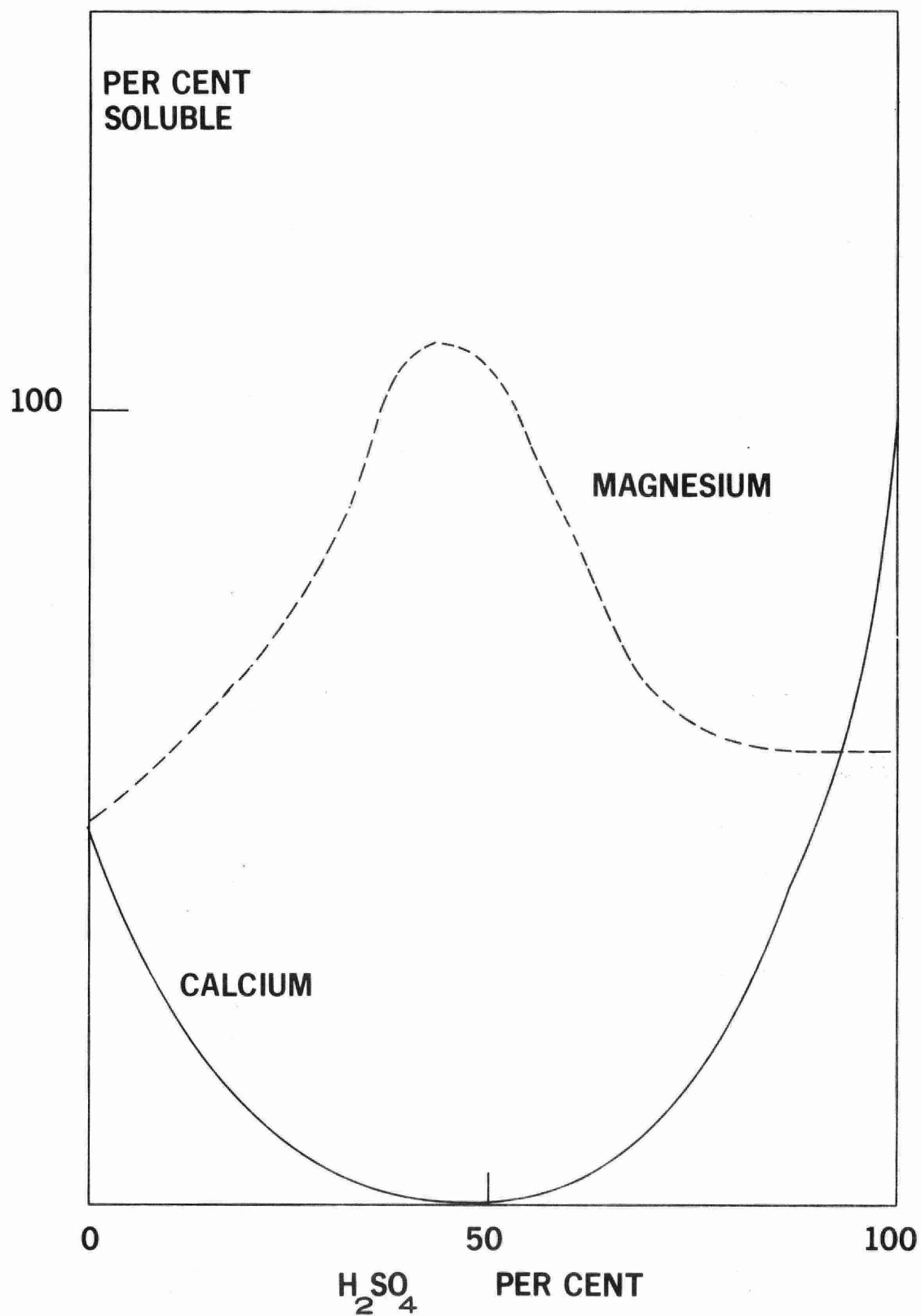


Figure 1: Solubility of Calcium and Magnesium in Aqueous Sulphuric Acid Solutions. Aqua Regia Solubility = 100%.

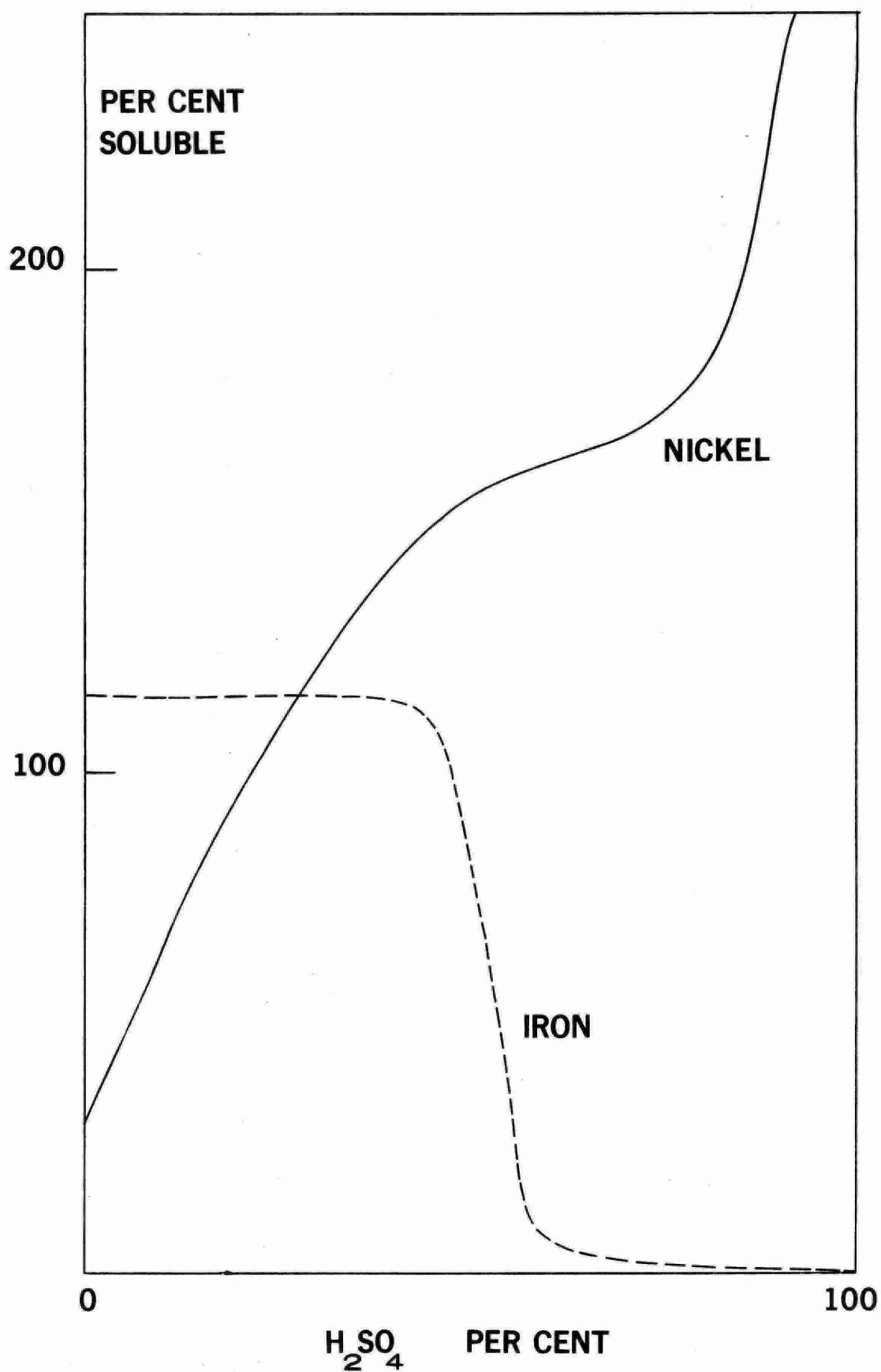


Figure 2 : Solubility of Iron and Nickel in Aqueous Sulphuric Acid Solutions.
Aqua Regia Solubility = 100%.

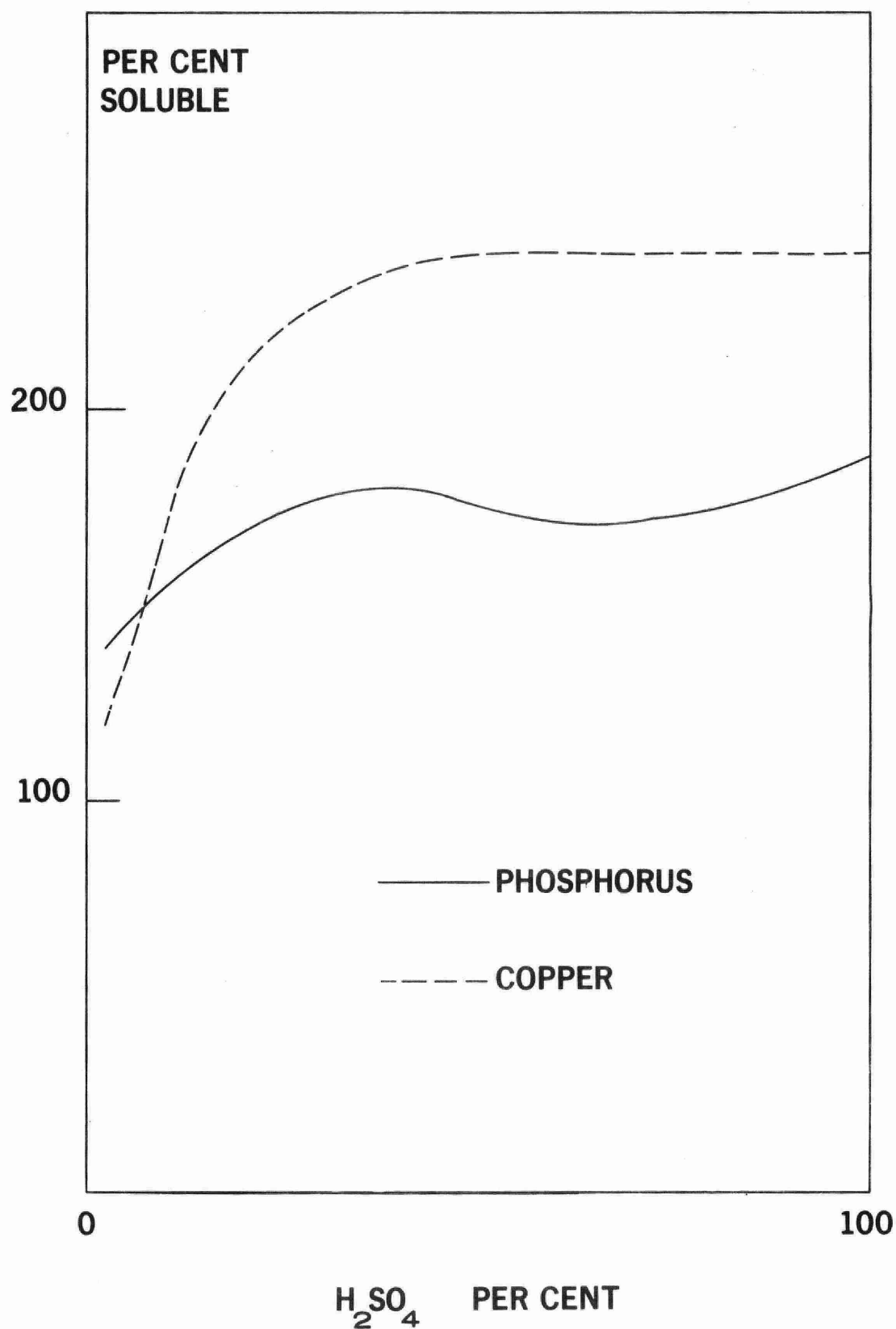


Figure 3: Solubility of Phosphorus and Copper in Aqueous Sulphuric Acid Solutions.
Aqua Regia Solubility = 100%.

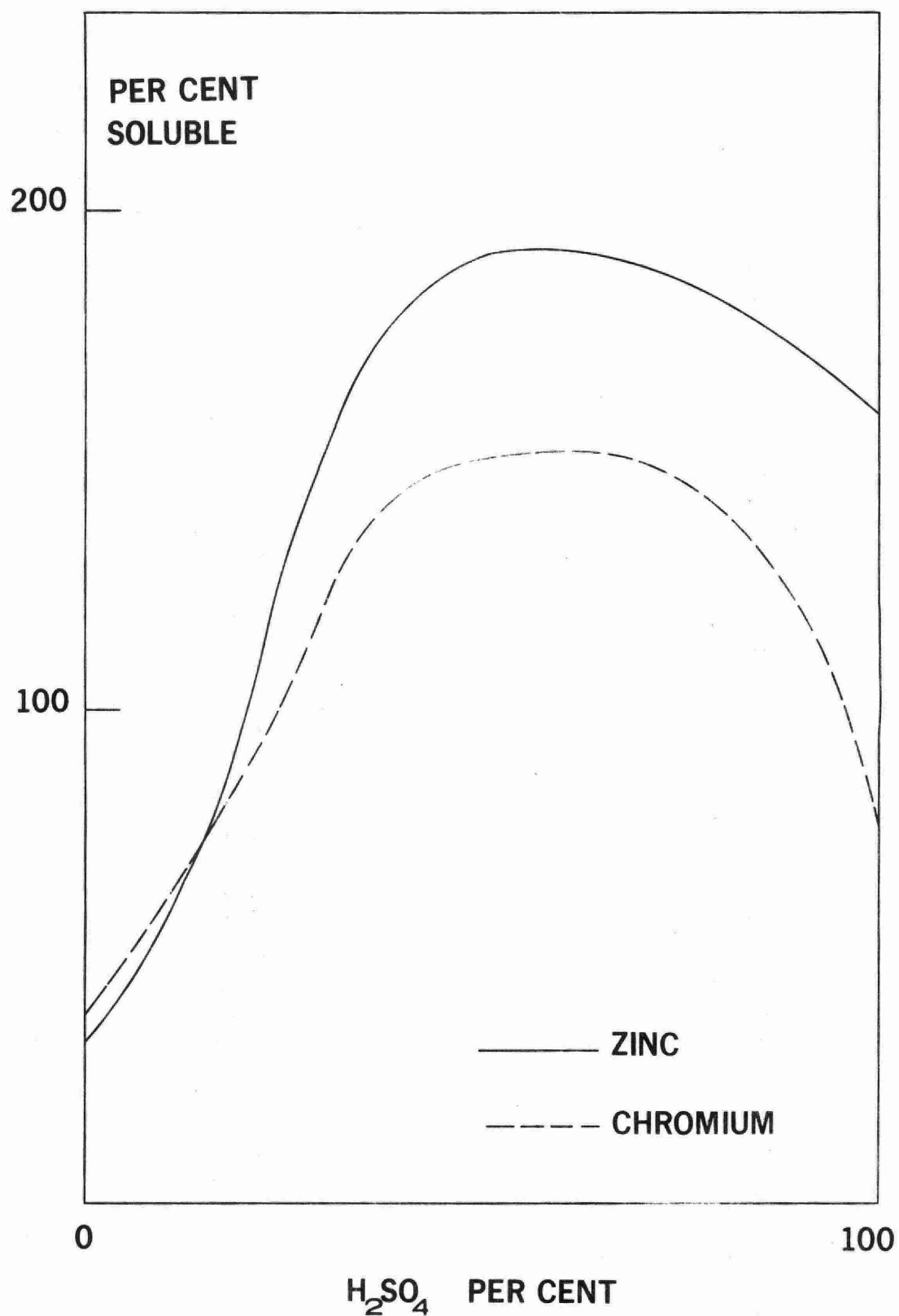


Figure 4: Solubility of Zinc and Chromium Recovery in Sulphuric Acid Solutions. Aqua Regia Solubility = 100%.

ash components. The efficiency of elemental recoveries are reported in terms of aqua regia solubilities in Table 8.

In general, the nitric-sulphuric mixtures behaved similarly to sulphuric acid-water mixtures. Magnesium, zinc and chromium showed similar tendencies: in both aqueous and nitric acid mixtures of sulphuric acid the solubility showed high maxima. However, the peaks were much broader when nitric acid was present (Figures 5-7).

Phosphorus and lead solubilities were not materially influenced by the addition of the oxidizing agent.

At sulphuric acid concentrations below 50%, the solubility of both copper and calcium was depressed in comparison with the aqueous sulphuric acid system. However, at higher H_2SO_4 concentrations the nitric acid present seemed to have very little influence on their solubility (Figures 8, 9).

The oxidizing effect of nitric acid was most efficient in solubilizing iron. The iron solubility was lowered at low sulphuric acid levels; however, above 50% H_2SO_4 concentrations the nitric acid mixture solubilized up to ten times as much iron as the aqueous mixture (Figure 10).

The effect on nickel solubility was reversed: the solubility of nickel decreased from 50% at 0% H_2SO_4 to 10% at 90% H_2SO_4 in the nitric acid system, even though in the aqueous system the solubility rapidly rose from 50% to 200% in the same sulphuric acid concentration range.

In general, the use of sulphuric acid-nitric acid mixtures showed very little advantage over the use of aqueous sulphuric acid solutions. The addition of nitric acid eliminated some of the preferential solubilities of sulphuric acids, thus limiting its use in metal recoveries. In analytical systems, aqua regia gave a much more powerful and more uniform effect with the exceptions of copper and zinc. These metals appeared to be more available to sulphuric-nitric leaching than to aqua regia leaching, especially when 50/50 w/w mixtures of the acids were used.

3.2.7 Solubility in sodium persulphate solutions

A 30% aqueous solution of sodium persulphate dissolved all elements with the exception of lead and calcium with an efficiency equal

TABLE 8

ASH SOLUBILITY IN SULPHURIC ACID-NITRIC ACID MIXTURES

CONCENTRATION OF SULPHURIC ACID	CONCENTRATION OF NITRIC ACID	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
100%	0%	92.5	75.8	120.9	0.7	57.0	94.1	17.2	178.3	92.0
90%	10%	69.0	149.0	152.7	13.7	56.8	10.4	12.4	183.7	67.0
75%	25%	47.7	169.8	120.1	48.4	72.0	16.1	13.6	195.9	69.0
50%	50%	2.0	171.0	128.3	93.1	109.6	34.9	11.4	204.3	78.0
25%	75%	0		33.2	65.1	87.9	43.0		166.7	
10%	90%	0		45.9	60.1	99.1	47.3		181.9	
0%	100%	45.5	37.4	49.5	40.7	47.2	28.2	49.5	32.7	66.6

All solubility figures are based on aqua regia solubility = 100%

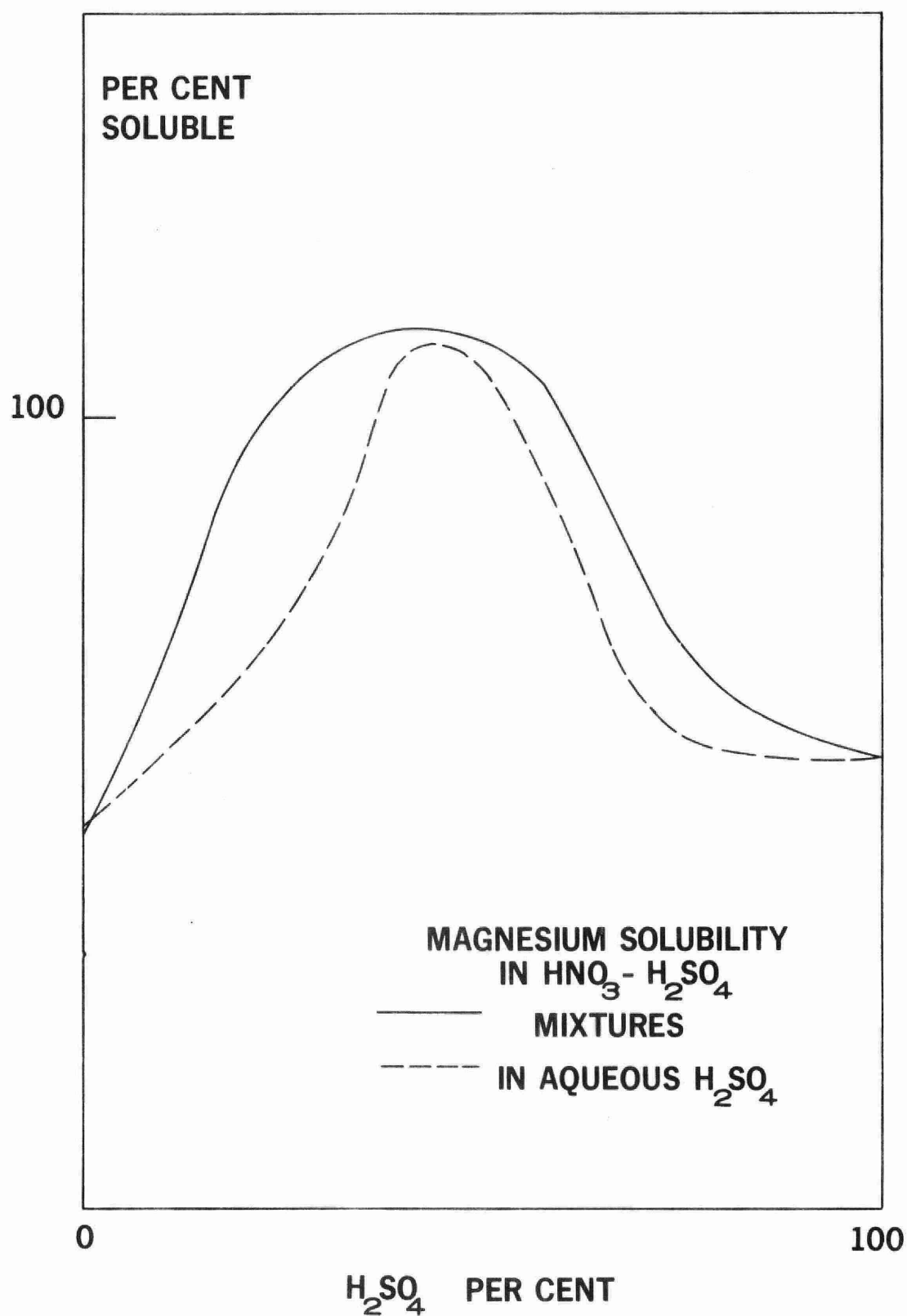


Figure 5: Solubility of Magnesium in Aqueous and Nitric Acid-Sulphuric Acid Mixtures. Aqua Regia Solubility = 100%.

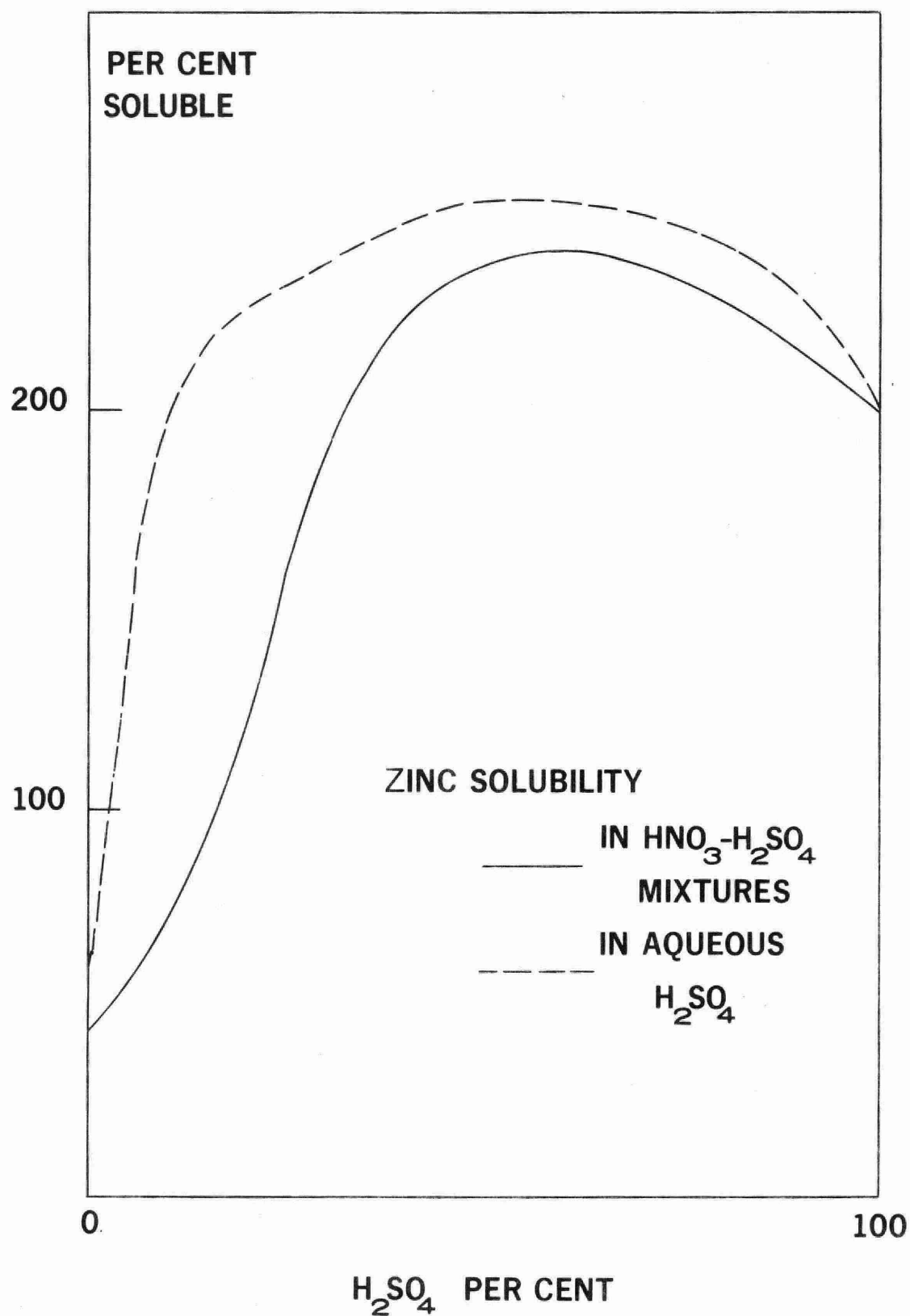


Figure 6: Solubility of Zinc in Aqueous and Nitric Acid-Sulphuric Acid Mixtures. Aqua Regia Solubility = 100%.

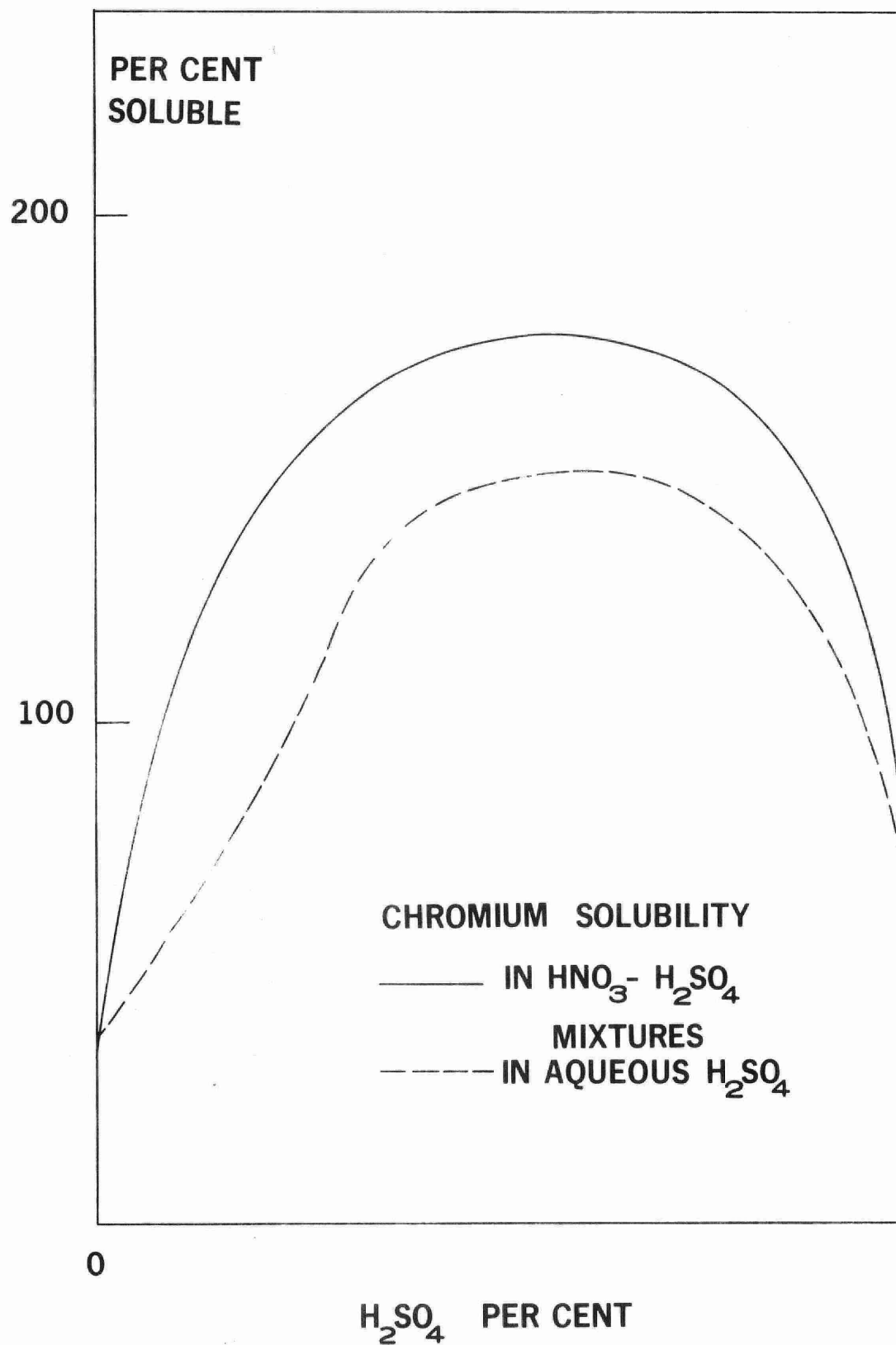


Figure 7: Solubility of Chromium in Aqueous and Nitric Acid-Sulphuric Acid Mixtures. Aqua Regia Solubility = 100%.

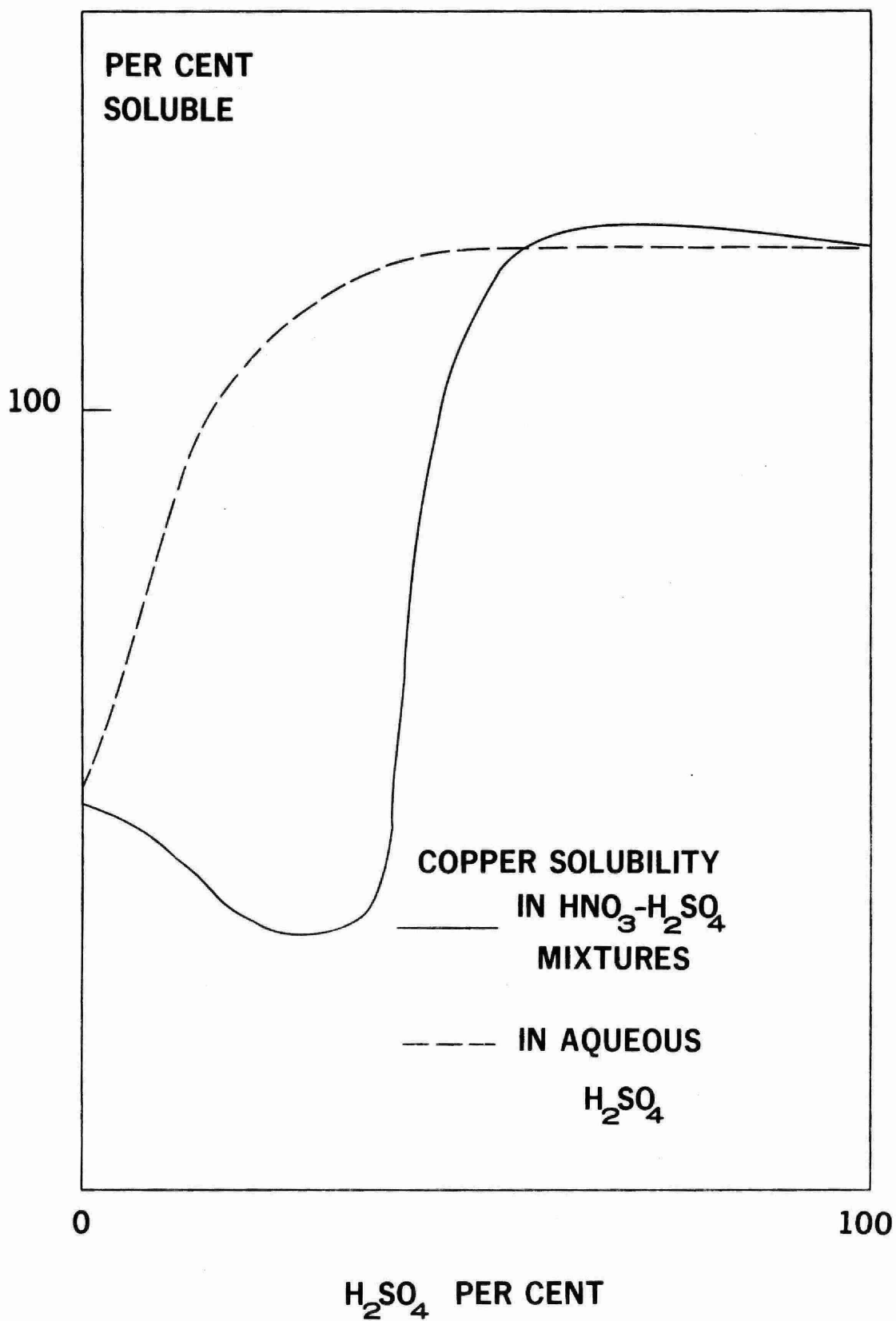


Figure 8: Solubility of in Aqueous and Nitric Acid-Sulphuric Acid Mixtures. Aqua Regia Solubility = 100%.

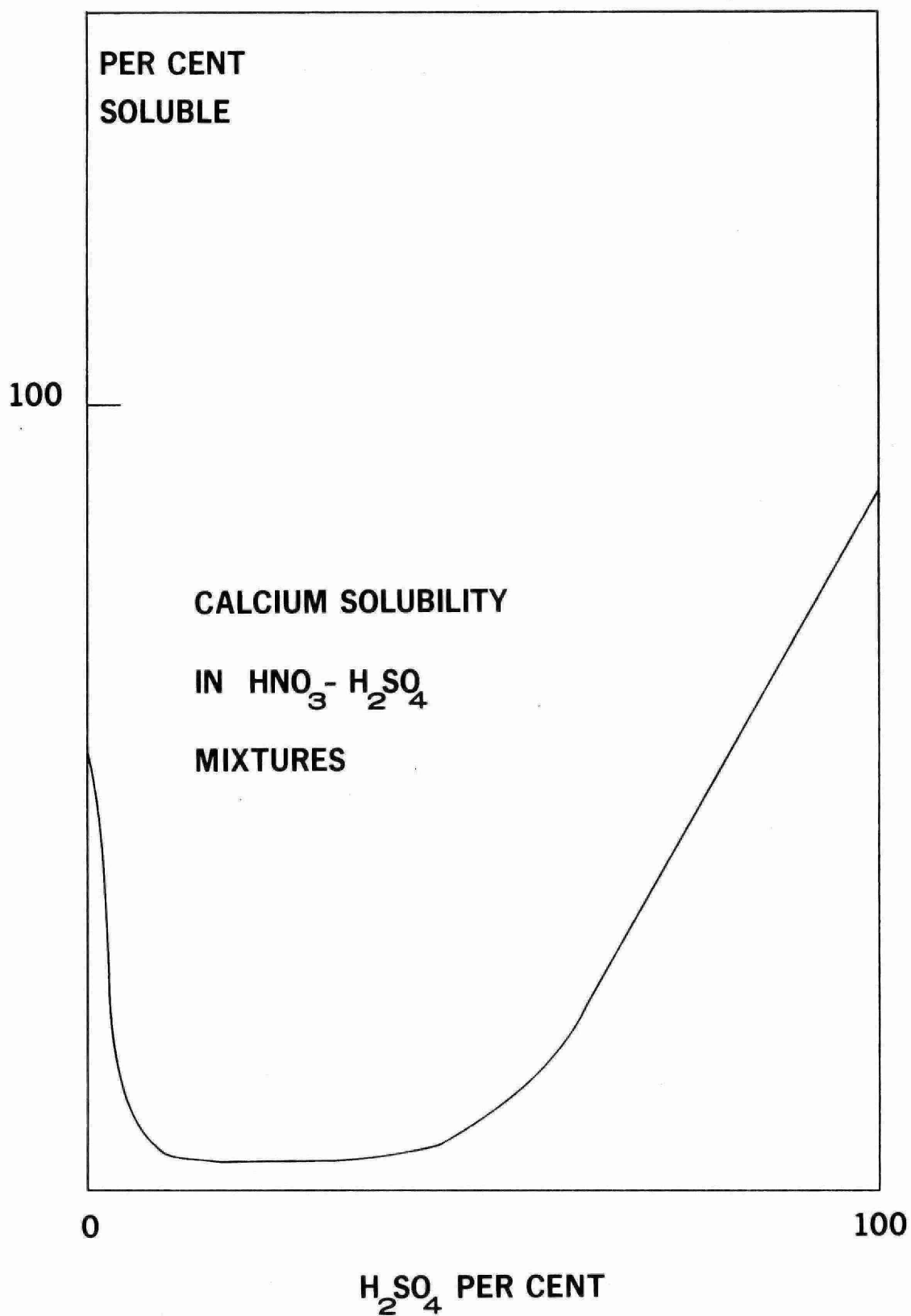


Figure 9: Solubility of Calcium in Nitric Acid-Sulphuric Acid Mixtures.
Aqua Regia Solubility = 100%.

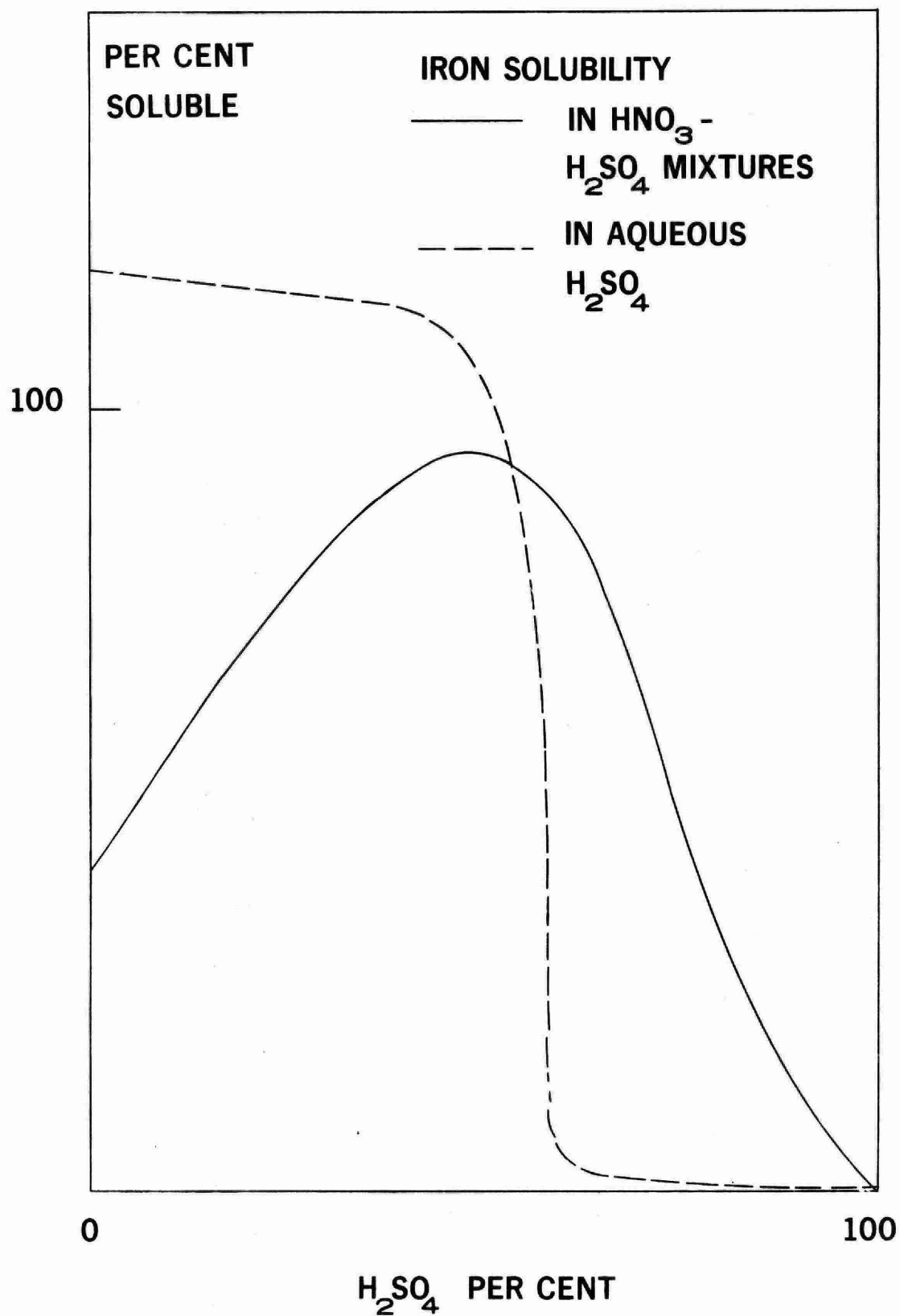


Figure 10: Solubility of Iron in Aqueous and Nitric Acid-Sulphuric Acid Mixtures. Aqua Regia Solubility = 100%.

to or greater than that of aqua regia. This prompted the investigation of the effects of smaller concentrations of sodium persulphate on ash solubility. The salt was dissolved in water (Table 9), concentrated sulphuric acid (Table 10) and 50% aqueous sulphuric acid (Table 11).

Aqueous persulphate solutions quickly lost their solvent efficiency below concentrations of 20%. Thus their use in a commercial system must be ruled out. While a 30% aqueous solution is very attractive for analytical purposes, its use in this capacity must be limited to systems where lead and calcium are of no interest.

These observations are even more applicable to sodium persulphate solutions in sulphuric acid. Solubility actually decreased with the addition of persulphate in most cases, thus the system is unsuitable for either analytical or recovery purposes.

When 50% aqueous sulphuric acid was used as the solvent for the sodium persulphate, considerably improved recovery efficiencies were observed. The addition of 1% persulphate increased the recovery of phosphorus and nickel, without materially affecting the solubility of the other components. 10% $\text{Na}_2\text{S}_2\text{O}_8$ generally increased the metal solubilities, with the notable exceptions of calcium and lead. Thus it may be practical to use this system for the efficient large scale solubilization of ash components. While there are no chemical disadvantages to this approach, the value of additional metal recoveries must be weighed against the additional chemical cost of the persulphate.

3.3 Separation Techniques

Several approaches were investigated, with the aim of either obtaining a set of valuable products or recovering inert, disposable solids. This segment of the work, naturally, contains less original data, since separations from a well defined single-phase liquid system are well understood, or at least homologous data is readily available. The purpose of these separations is only to demonstrate feasibility, since the viability of all but the most exotic systems can only be determined on the basis of costs after chemical and energy recoveries. To obtain valuable economic data, some small scale pilot plant work must be done.

TABLE 9

SOLUBILITY OF ASH IN AQUEOUS SODIUM PERSULPHATE

<u>CONCENTRATION OF $\text{Na}_2\text{S}_2\text{O}_7$</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
5%	17.5	5.8	46.2	12.6	76.6	14.5	7.6	9.2	59.9
10%	19.1	14.2	60.5	28.6	87.2	27.0	8.6	22.6	85.1
20%	17.0	34.9	68.6	45.3	77.7	49.3	7.8	34.2	86.8
30%	13.9	129.3	111.6	90.3	119.3	105.2	5.9	168.3	96.2

All solubility figures are based on aqua regia solubility = 100%

TABLE 10

SOLUBILITY OF ASH IN SULPHURIC ACID-SODIUM PERSULPHATE SOLUTIONS

CONCENTRATION OF $\text{Na}_2\text{S}_2\text{O}_7$ IN CONC. H_2SO_4	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
0%	92.5	75.8	120.9	0.7	57.1	94.1	17.2	178.3	92.4
1%	67.0	16.3	100.3	1.6	37.3	104.3	13.1	111.0	70.2
5%	66.2	19.3	83.9	1.6	25.9	101.6	15.9	114.2	70.6
10%	56.6	7.3	87.4	2.4	25.3	84.2	13.6	77.1	60.1
20%	80.6	54.0	85.2	3.9	15.6	101.3	15.9	71.3	68.6

All solubility figures are based on aqua regia solubility = 100%

TABLE 11

SOLUBILITY OF ASH IN AQUEOUS SULPHURIC ACID-SODIUM PERSULPHATE SOLUTIONS

CONCENTRATION OF
 $\text{Na}_2\text{S}_2\text{O}_7$ IN 50% AQUEOUS
 H_2SO_4

	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
0%	0.3	143.3	122.9	110.0	109.7	39.7	3.9	167.1	74.3
1%	0.0	139.0	112.6	110.1	104.3	55.6	2.6	132.0	80.2
5%	0.0	126.5	100.4	99.5	93.9	44.1	1.6	131.6	70.2
10%	0.0	168.1	122.9	118.8	115.3	44.1	2.3	148.1	84.0
20%	0.0	134.3	105.6	102.4	100.0	40.5	1.9	136.8	72.4

All solubility figures are based on aqua regia solubility = 100%

The evaluation of these system is difficult, since a value should be attached to the improvement of the environment by decreased leaching of potentially harmful substances.

3.3.1 Ash fusion

The high metal values obtained with sulphuric acid indicate that some of the heavy metals are tied up in forms not available for aqua regia leaching. There were indications that some refractory metal oxides in the ash may not be leachable with any of the solvents tried in section 3.2. With some modification of the present incineration processes, the character of the ash may, possibly, be altered to produce a less intractable ash. In order to obtain a more soluble ash form, the ashes were fused with sodium carbonate, sodium persulphate and sodium hydroxide in a series of experiments.

Although boiling of the ashes with aqueous sodium carbonate did not solubilize any of the ash components to an appreciable extent, fusion at 850-900°C resulted in a melt that was partially water soluble. After filtration, the residue released practically all of its metal and phosphate content in acetic acid (Table 12). Since the separation of metals from acetic acid solution was investigated by Burrow and Webber (1972), this approach was not attempted.

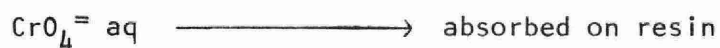
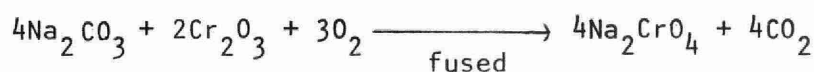
Two important points are immediately obvious on examining the data. Apparently a large fraction of the chromium is normally bound up in refractory chromia, and it was therefore not detected by acid digestion. This chromium was released by sodium carbonate fusion, as a water soluble salt. Aside from sodium, chromium was the only water soluble metal present to any degree in the system, suggesting a simple, and possibly economical recycle system: recarbonate the excess sodium from the fusion process by the possible use of carbon dioxide recovered from the incinerator fluegases, and remove the chromium, for further concentration, by a specific ion exchange system. A system for the recovery of chromium by ion exchange is commercially available from the Wix Corporation. The system uses resins readily available from Rohm and Haas Inc. The chemistry of this reaction sequence may be summarized by the following equations.

TABLE 12

SODIUM CARBONATE FUSED ASHES: TYPICAL METAL DISTRIBUTION

<u>TREATMENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
Water soluble portion µg/g ash	28	6930	4	32	12	65	0.0	0.0	17500
Acetic Acid soluble from residue µg/g ash	62700	1660	3980	23400	9120	305	1480	6540	354
HCL soluble from residue µg/g ash	50200	862	1050	25800	6540	226	1340	4360	35800
	_____	_____	_____	_____	_____	_____	_____	_____	_____
TOTAL *	112900	9450	5030	49200	15700	598	2820	10900	53700
	=====	=====	=====	=====	=====	=====	=====	=====	=====

* Totals rounded to appropriate number of significant digits



The water insoluble residue may be disposed, as it is presently done, since its activity has not been materially altered.

Alternately, further treatment, using mineral acids may be considered, as outlined in section 3.3.4.

As expected, sodium hydroxide fusion yielded essentially identical results to sodium carbonate fusion. Thus a simplified chromium recovery system may be also used where the alkaline effluent from the cation exchanger may be directly recycled to the incinerator.

Sodium persulphate fusion did not prove to be valuable, since solubilities were very similar to those obtained directly by aqueous sodium persulphate (Table 13). Surprisingly, none of the fusion processes released any aluminum as a soluble salt. In all cases, aluminum concentrations remained below 100 µg per gram of ash treated.

In summary, fusion processes release some heavy metals bound as refractory oxides. Thus, if the economic value of the released chromium or nickel warrants it in certain plants, some alternation in the incineration system may be justified to allow their recovery. While the fusion releases some excesses in other elements, there is no advantage in their removal, since they are present in an ecologically safe, permanent form.

3.3.2 Zinc and phosphorus recovery process

Aqueous sodium hydroxide displaced a large proportion of phosphates, and solubilized them as sodium phosphate (Table 6). Approximately 64% of the phosphorus present is readily recoverable even during a single stage contact. Higher total recoveries may be expected in a multistage extraction or a counter-current continuous extraction of ashes with NaOH solutions.

As shown by Table 6, the sodium hydroxide did not dissolve any of the metals to an appreciable extent, with the exception of zinc. As expected, more than half of the zinc present was transformed into

TABLE 13

COMPARISON OF FUSION SYSTEMS: WATER SOLUBILITY OF FUSED MASS

<u>TREATMENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
NaOH fusion	0.0	198.2	1.2	0.1	0.0	33.2	3.2	1.7	37.6
Na ₂ S ₂ O ₇ fusion	48.1	162.5	130.6	92.6	127.6	174.0	29.8	170.1	61.3
Na ₂ CO ₃ fusion	0.0	165.9	0.2	0.2	0.2	21.4	0.0	0.0	31.1

Solubility in aqua regia = 100%

soluble sodium zincate. Curiously, aluminum did not solubilize as the aluminate; in all cases the aluminum was tied up as the refractory oxide and less than 300 µg was recoverable per gram of ash. As in the case of the phosphorus, the zinc recovery may be increased by increasing the number of extraction steps.

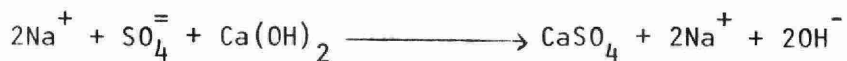
Separation of this three component system does present some difficulties: sodium phosphate is not readily recoverable without neutralizing the excess sodium hydroxide. The market for sodium phosphate is not very promising, as the fertilizer manufacturers generally avoid sodium ash.

Thus, there is little future in neutralizing the excess hydroxide with nitric acid, as the product, although rich in both nitrate and phosphate, is unsuitable or undesirable in most applications as a fertilizer. Alternately, the sodium phosphate is suitable as a detergent raw material. However, this usage is rapidly diminishing because of the resultant high phosphate content of domestic sewage.

Other treatment alternatives include recovery of phosphoric acid or calcium phosphate. The zinc content of the solution may be recovered on weak cationic resins after suitable dilution. After this point, essentially a two component system results: aqueous sodium phosphate and sodium hydroxide.

The phosphates may be removed on an anion exchange resin, where OH^- groups may be exchanged for PO_4^{3-} ions. This exchange must be carried out at relatively low OH^- concentrations. The phosphate may be eluted by H_2SO_4 and recovered by distillation as the acid. The column can be regenerated with NaOH , and the excess sulphates removed as CaSO_4 by lime addition. This rather complicated system relies on the very low cost of sulphuric acid, and the relatively low cost of NaOH . The reaction sequence may be summarized as follows:





The practicality of this approach depends very much on the capacity and the stability of the anion exchange resin. If a high percentage of the exchange sites can be filled with phosphate ions, the cycle will be economical, since the cost of lime, sulphuric acid and lost NaOH should amount to less than 2¢ per pound of H_3PO_4 produced, while its value is in the excess of 10¢ per pound. The operating margin, which must absorb all capital and energy costs, is some \$36.00 per ton of ash. This value will be used up very rapidly if the resin is deteriorated by the harsh conditions within the cycle.

Perhaps the most economical recovery system would involve the reaction with lime to form calcium sulphates that are, in the partially acidified form, excellent fertilizers. Pilot work should be conducted on this cycle since accurate control of kinetic conditions could lead to a viable commercial system.

The caustic washed ash still contains heavy metals in fairly high concentrations and their disposal presents problems identical to that of the untreated ash. An acid wash should be included, therefore, in the complete treatment cycle.

3.3.3 Phosphoric acid recovery

Phosphoric acid was found to be an excellent solvent for all ash components except copper and zinc (Table 5). Since phosphorus is the most valuable component of the ash, this prompted the investigation of a phosphoric acid based recovery cycle. Initial ideas of ion exchange removal of all metals had to be abandoned due to the excessive viscosity of the system. At temperatures below 120°C , the ash-phosphoric acid mixture gelled completely and the viscosity had to be lowered by 50-75% water addition. Partial precipitation of calcium phosphate at these dilutions created further problems.

Attempts were made to remove the bulk of the metal ion content of the solution by the addition of concentrated sulphuric acid. This

resulted in the precipitation of calcium sulphate, and the hydrolysis of the metal phosphates to phosphoric acid.

The separation of the resulting multicomponent system presented many difficulties. Phosphoric acid cannot be purified by distillation, as it breaks down by several dehydration steps. In commercial practice, phosphate rock, (essentially calcium phosphate), is hydrolyzed to phosphoric acid by sulphuric acid addition. The calcium sulphate produced is removed by filtration, and the excess sulphuric acid is removed by vacuum distillation. While this procedure may be used with the ashes, the heavy metal content, with the exception of the precipitated calcium, will remain with the phosphoric acid produced.

Two methods for the removal of these contaminant metals were investigated: liquid-liquid extraction, and ion exchange.

Phosphoric acid is quite soluble in a 3:1 mixture of methanol and ether. Thus phosphoric acid may be recovered and concentrated from dilute aqueous solutions. In this investigation it was found that the phosphoric acid had been very effectively concentrated in the organic phase, however some sulphuric acid and associated sulphate salts also moved into the organic solvent. In these experiments, the calcium content of phosphoric acid was reduced by a factor of 40 - 100,000 by the acid hydrolysis, filtration, liquid-liquid extraction sequence.

Since the partition coefficient in this extraction strongly favours the separation of phosphoric and sulphuric acids, multiple extractions or continuous countercurrent extraction will yield good quality phosphoric acid.

The separation of the solvent from the phosphoric acid is simplified by the low boiling point of the mixture. However, its extreme flammability requires considerable care in equipment design and operation. While distillation of ether is quite safe in a closed system, great care must be taken when such a process is introduced to an industry that is not familiar with the usual hazards of a petrochemical plant. To avoid this difficulty, a large series of non-polar solvents were examined, without success. None of the "safer" solvents, such as carbon tetrachloride, chloroform, isobutyl alcohol, MIBK etc. was suitable for partition.

Ion exchange may also be used for the purification of crude phosphoric acid. In this case, the heavy metals in the mixture must be exchanged for hydrogen ions by a cation exchanger. While this operation is theoretically very simple, it requires the dilution of the acid mixture before contacting the column. The final dilute phosphoric-sulphuric acid mixture is concentrated and separated by vacuum distillation.

The metal salts may be eluted from the column at increased concentrations by a strong acid, preferably sulphuric acid. Further separation or disposal may be by standard wet chemical methods outlined in section 3.3.4.

3.3.4 Sulphide precipitation

Once the heavy metal content of the ash has been concentrated on an ion exchange column, the metals must be removed in an environmentally safe manner. The metals may be eluted by either hydrochloric or sulphuric acid, and then selectively precipitated. The classical, analytical separation seems most suitable: the heavy metals are precipitated as sulphides from slightly acid or alkaline media. Lead and copper sulphides are removed at low pH. After filtration, the solution is neutralized by sodium or preferably ammonium hydroxide. At the higher pH values, nickel sulphide precipitates together with chromium hydroxide and zinc sulphide. Further separation may be best effected by the standard metallurgical separation techniques. Thus in effect, all the major heavy metals may be recovered, and recycled as "artificial ores".

The "effluents" from this treatment stage would be a dilute sodium sulphate-magnesium sulphate solution that, at the relatively low levels produced, will be environmentally acceptable.

4. PILOT PLANT PRELIMINARY DESIGN

Figure 11 shows the reaction sequences for the various recovery processes discussed in the previous section. The main reaction sequence was selected for a preliminary process flowsheet (Figure 12). The process consists of ash digestion by 60% H_2SO_4 , followed by metal recovery in an ion exchange column and phosphoric acid recovery by vacuum distillation of sulphuric acid. The trapped metals are eluted by sulphuric acid and precipitated as sulphides.

The process has the obvious disadvantage of the necessity to evaporate a large volume of water, however waste heat recovery may reduce the extent of this problem.

A preliminary cost estimated for a plant treating 300 lb ash/hour would include the following:

1	Stainless steel reactor, 500 gal	\$ 20,000.00
2	FRP reactors, 500 gal	\$ 4,400.00
1	Ion exchange column	\$ 2,100.00
1	Stainless steel condenser	\$ 2,800.00
3	Polypropylene filter presses	\$ 18,600.00
1	Ash feeder	\$ 1,200.00
3	Mixers	\$ 1,250.00
7	Pumps - corrosion resistant slurry pumps	\$ 7,600.00
5	Reagent tanks, FRP	\$ 4,250.00
CAPITAL EQUIPMENT Sub Total		\$ 62,200.00
Piping at 15%		\$ 9,300.00
Instrumentation at 20%		\$ 12,500.00
Engineering at 15%		\$ 12,600.00
Installation at 20%		\$ 19,300.00
TOTAL CAPITAL COST		\$115,900.00

While this cost is very high for a production plant in terms of the recoverable value, the pilot plant includes considerable instrumentation and flexibility to permit a wide range of process variables.

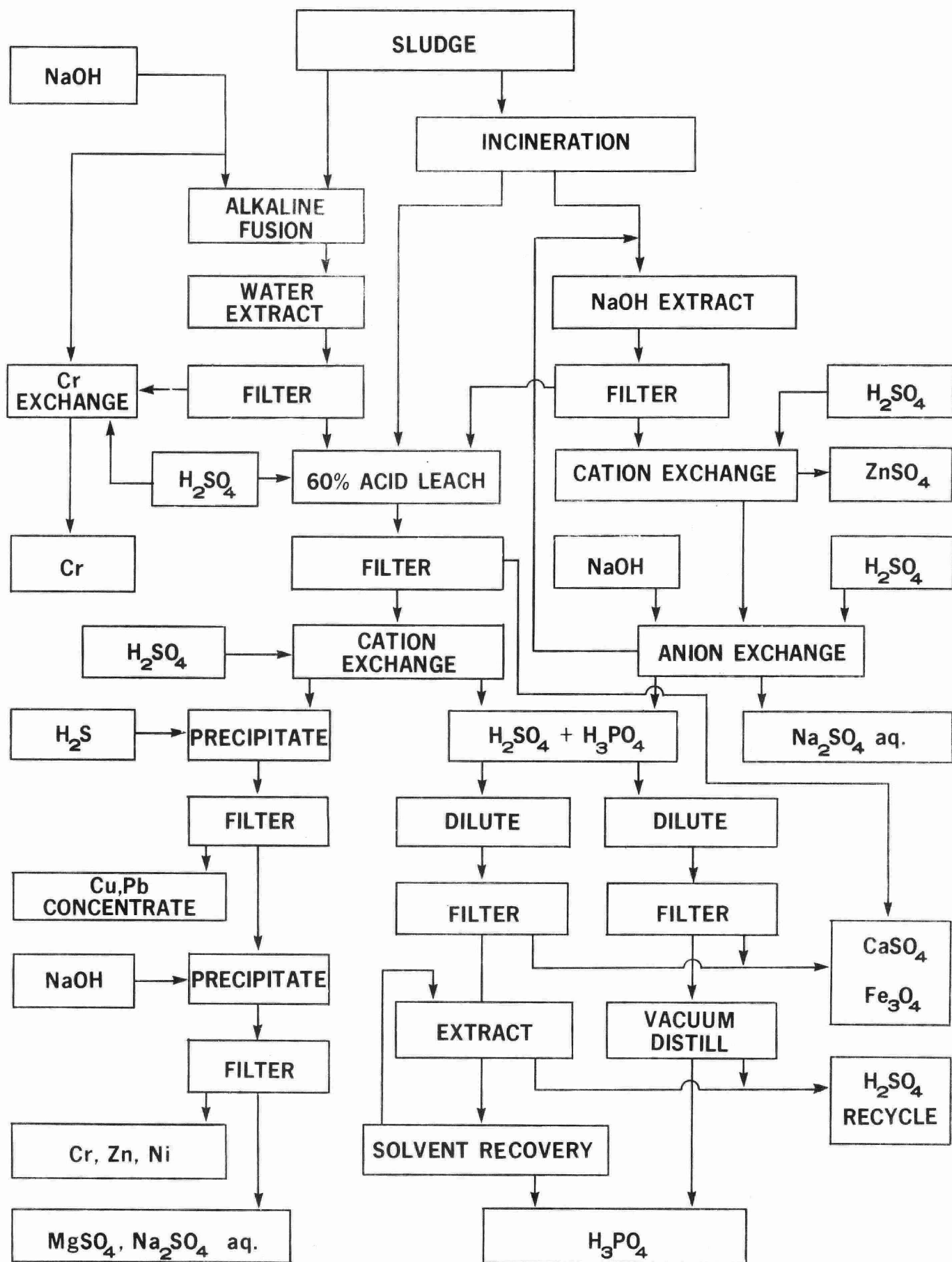


Figure 11: Process Flow Diagram.

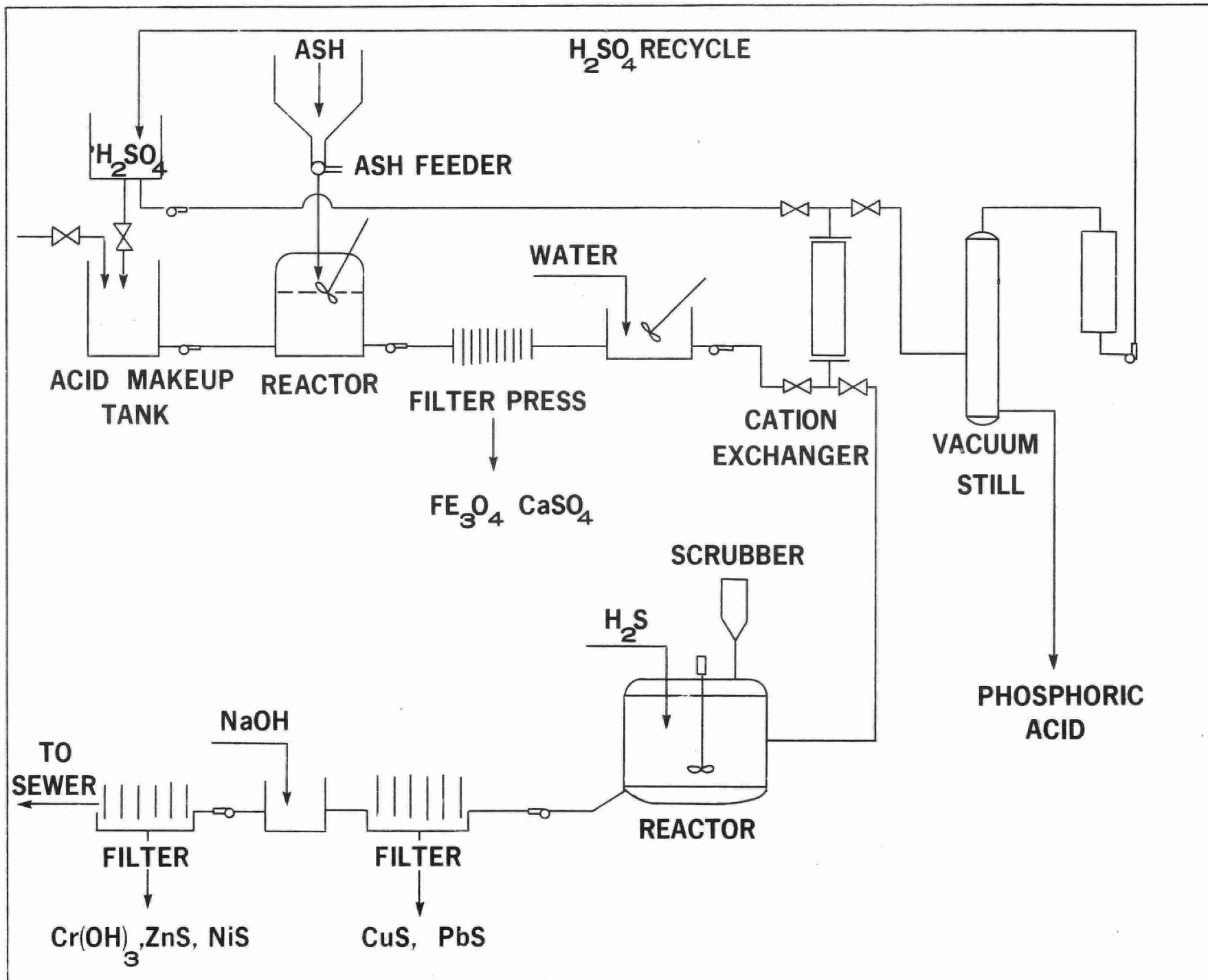


Figure 12: Pilot Plant Preliminary Process Flow Sheet.

Since sewage treatment plants do not have adequate chemical experience, and the volume of phosphoric acid recovered is limited, the production of crude phosphoric acid should be considered for sale to a major producer who may then purify and use the acid on a more economical scale. The process flowsheet will then be simplified, as shown on Figure 13. The current cost of phosphoric acid is approximately 12¢/lb, and therefore a price of 8¢/lb may be expected. On this basis the margin based on chemicals will be approximately 5¢/lb or \$550/day.

A very rough estimate of major equipment includes:

Tanks		\$ 8,000
Pumps		\$ 15,000
Reactors		\$ 30,000
Filters		\$ 60,000
Distillation		\$ 80,000
Grinder		\$ 30,000
		\$223,000
Installed cost	Appr.	\$450,000

The potential gross revenue of phosphoric acid recovery from a 100 MGD sewage treatment plant is approximately \$320,000 per annum, at current prices. Chemical costs represent some \$100,000 per annum allowing some \$220,000 for operating costs and amortization of capital equipment. While the potential profits are marginal, a closer look into this and other recovery processes is warranted.

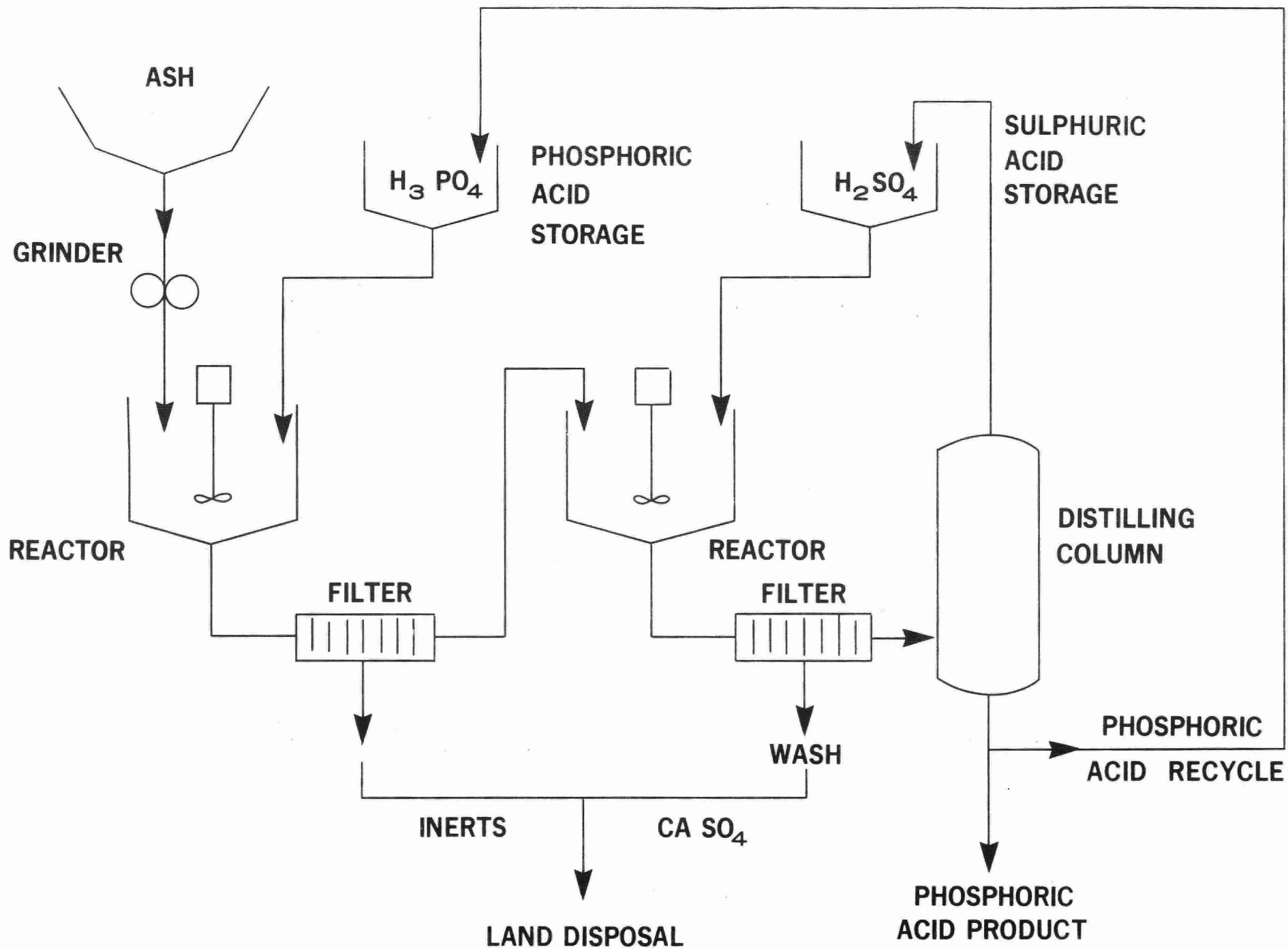


Figure 13 : Proposed Raw Phosphoric Acid Recovery System.

Despite the preliminary nature of this study, several important conclusions were reached.

The data indicate that heavy metals leach out of the ash even with neutral distilled water. On prolonged contact (2-3 hours) approximately 1 mg/l chromium has been measured in the water. Since natural waters are often acidic, considerably higher leaching rates might be expected. The potential of environmental contamination by heavy metals warrants a closer examination of ash disposal methods, and may provide a non-economic incentive to ash recycling.

Aluminum and iron sulphates are chemicals added during sewage treatment. Their recovery would be of great benefit and convenience to sewage treatment plant operations. This study found this approach to be uneconomical, as was predicted. Iron was present at relatively low levels of about 4-5%. Magnetic iron oxide was present but iron recovery from this form is impractical, since the cost would be several times higher than the commercial cost of ferrous sulphate.

Similarly, aluminum was present in the form of a refractory oxide that is not responsive to any inexpensive chemical treatment. While the recovery of these flocculents may be possible, recovery must be made before the formation of intractable oxides by incineration.

The analyses of the ash revealed that the variable composition of the sewage was exaggerated in the incinerated ash. The ash was highly inhomogeneous, especially in the heavy metals. The composition changed very rapidly, on a time scale of a few minutes; however, the overall characteristics of the ash remained fairly constant. A mass balance, based on all the ash analyses is presented in Table 14.

Approximately 50% of the ash was in the chemically inert form of silicates and alumina. This study found that a large proportion of all heavy metals, especially zinc and chromium was physically or chemically bound by these refractories, which are not available through acid digestion. When these compounds were released by alkaline fusion, analyses of the ten major ash components gave a mass balance of 98%.

The presence of 20-50% strongly bound heavy metals in the ash suggests that perhaps the simplest approach to safe ash disposal may be

TABLE 14

COMPOSITION AND VALUE OF ASH

MEASURED COMPONENT	WEIGHT $\mu\text{g/g}$ ASH	PROBABLE FORM	WEIGHT $\mu\text{g/g}$ ASH	RECOVERABLE FORM	WEIGHT lb/ton ASH	VALUE/TON ASH
Ca	114,000	$\text{Ca}_3(\text{PO}_4)_2$	294,000	none	N/A	---
Cr	9,280	Cr_2O_3	27,100	$\text{Cr}(\text{OH})_3$	36.8	\$19.00
Cu	3,780	$\text{Cu}_3(\text{PO}_4)_2$	7,550	CuS	11.4	\$3.00
Fe	49,200	Fe_3O_4	68,000	none	N/A	---
Mg	15,900	$\text{Mg}(\text{PO}_4)_2$	78,000	none	N/A	---
Ni	532	Ni_2O_3	970	NiS	1.6	\$0.80
Pb	2,320	$\text{Pb}_3(\text{PO}_4)_2$	3,030	PbS	5.4	\$0.30
Zn	11,200	$\text{Zn}_3(\text{PO}_4)_2$	22,100	ZnS	33.4	\$3.40
Al	58,000	Al_2O_3	93,000	none	N/A	---
SiO_2	385,000	SiO_2	385,000	none	N/A	---
S	700	M_2SO	2,080	none	N/A	---
P	56,300	---	---	H_3PO_4	356	\$46.50
TOTAL	706,000		981,000			\$73.00

in the formation of refractories from all ash components. By the addition of some fluxing agents, or by altering the incinerator conditions, it may be possible, and beneficial, to produce a glasslike "ash" that will contain much lower quantities of leachable heavy metals than the present ash.

Phosphorus represents the highest economic value in the ash. It is present to the extent of 14-18% expressed as phosphoric acid. Since practically all of Canada's phosphorus is imported as phosphate rock, the recovery of the phosphate seems most advantageous. Recently the price of phosphate rock has increased considerably on the international market, and the phosphate value of the ash is currently some \$46.00 per ton.

Phosphorus is readily solubilized by either phosphoric or 60% sulphuric acids. The use of H_2SO_4 permits the removal of the inert calcium sulphate and iron oxides. The remaining heavy metals must be removed by ion exchange if metal free phosphoric acid is to be recovered by sulphuric acid distillation. Another alternative would remove the phosphoric acid by liquid-liquid extraction followed by solvent recovery.

The metal content of the leaching liquor may be concentrated by ion exchange, and recovered by sulphide precipitation. The extremely low dissociation product of heavy metal sulphides provides perhaps the most efficient removal of these metals from water.

Chromium or zinc may be concentrated by special procedures where the total quantity present in the ash warrants it.

In summary, only phosphate recovery seems economically warranted. However, the study of recovery processes should be expanded, since there are indications that the ash in its present form may contribute to the heavy metal loading of groundwater.

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APPENDIX

ANALYTICAL RESULTS

TABLE 15.1
WATER SOLUBILITY OF ASHES

<u>ELEMENT</u>	<u>SAMPLE 1</u> <u>µg/g ash</u>	<u>SAMPLE 2</u> <u>µg/g ash</u>	<u>SAMPLE 3</u> <u>µg/g ash</u>
Ca	3832	2838	3029
Cr	17	18	18
Cu	0.8	0.2	--
Fe	0.4	0.2	--
Mg	622	454	487
Ni	--	--	--
Pb	--	--	--
Zn	5	2	2
P	54.4	10.9	10.3

TABLE 15.2

SOLUBILITY OF SEWAGE SLUDGE ASH

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
D5	AQUA REGIA	85,500	3,880	1,850	31,400	9,950	252	1,560	4,740	46,200
D6	AQUA REGIA	108,500	3,660	2,250	38,600	12,300	311	1,680	5,640	56,000
D7	AQUA REGIA	103,000	4,600	2,200	38,300	11,900	287	1,620	5,350	55,300
D8	AQUA REGIA	103,000	4,540	2,220	39,300	12,000	303	1,740	6,990	55,300
D9	AQUA REGIA	101,000	4,390	2,220	39,000	13,100	316	1,580	6,530	59,200
D10	AQUA REGIA	103,000	3,710	2,130	38,900	11,900	303	1,570	5,100	55,900

TABLE 15.3

SOLUBILITY OF SEWAGE SLUDGE ASH

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
16-2	AQUA REGIA	93,600	3,120	1,850	29,900	12,200	457	1,510	3,640	53,000
16-3	AQUA REGIA	89,000	2,800	1,770	32,100	11,500	556	1,610	3,090	53,400
A11	AQUA REGIA	84,200	3,880	2,150	32,400	13,000	572	2,600	4,770	51,000
A12	AQUA REGIA	82,200	4,150	2,030	31,800	13,000	570	1,310	4,960	53,300

TABLE 15.4

SOLUBILITY OF SEWAGE SLUDGE ASH

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
E1	100% H_2SO_4	80,800	2,500	2,320	265	7,070	555	291	6,830	46,300
E2	100% H_2SO_4	80,700	2,780	2,400	161	7,120	458	313	7,840	51,000
A1	90% H_2SO_4 10% HNO_3	58,900	4,620	2,290	4,770	6,950	48	224	7,550	31,800
A2	90% H_2SO_4 10% HNO_3	61,500	5,770	3,670	3,850	7,170	63	215	7,560	39,000
A3	75% H_2SO_4 25% HNO_3	46,000	6,800	2,320	15,400	8,800	84	244	8,780	34,500
A4	75% H_2SO_4 25% HNO_3	37,300	5,040	2,370	15,200	9,100	90	237	7,340	38,200

TABLE 15.5

SOLUBILITY OF SEWAGE SLUDGE ASH

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
A5	50% H ₂ SO ₄ 50% HNO ₃	2,180	5,670	2,480	31,200	13,400	184	199	8,660	41,600
A6	50% H ₂ SO ₄ 50% HNO ₃	1,350	6,250	2,530	27,500	13,900	192	202	8,150	40,700
D1	50% H ₂ SO ₄ 50% HNO ₃	87	5,910	2,520	6,290	12,600	361	116	8,150	57,400
D2	50% H ₂ SO ₄ 50% HNO ₃	83	4,710	2,260	5,600	10,700	338	113	7,700	51,700
D3	50% H ₂ SO ₄ 50% HNO ₃	82	5,270	2,370	6,250	11,600	369	139	7,500	53,500
D4	50% H ₂ SO ₄ 50% HNO ₃	83	4,350	2,560	6,010	13,000	388	132	8,450	59,700
18-8	100% HNO ₃	39,600	1,300	966	12,800	5,870	152	871	1,340	35,100

TABLE 15.6

SOLUBILITY OF SEWAGE SLUDGE ASH

SAMPLE NUMBER	SOLVENT	Ca	Cr	Cu	Fe	Mg	Ni	Pb	Zn	P
E1	100% H ₂ SO ₄	80,800	2,500	2,320	265	7,070	555	291	6,830	46,300
E2	100% H ₂ SO ₄	80,700	2,780	2,400	161	7,120	458	313	7,840	51,000
C1	80% H ₂ SO ₄	50,100	5,740	2,330	298	7,830	1000	255	8,080	46,900
C2	80% H ₂ SO ₄	50,900	3,930	2,180	293	6,600	936	335	7,830	42,200
C3	70% H ₂ SO ₄	6,090	6,180	2,330	855	7,940	893	187	7,730	42,800
C4	70% H ₂ SO ₄	7,410	5,380	2,370	848	7,690	868	137	7,440	45,300
C5	60% H ₂ SO ₄	509	5,780	2,320	2,340	11,700	828	111	7,700	42,900
C6	60% H ₂ SO ₄	603	4,580	1,890	2,080	10,700	834	108	8,210	44,700

TABLE 15.7

SOLUBILITY OF SEWAGE SLUDGE ASH

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
C6	50% H ₂ SO ₄	277	4,990	2,400	34,700	13,600	214	69	6,870	39,200
C7	40% H ₂ SO ₄	1,210	4,180	2,060	32,400	13,800	818	101	7,620	46,600
C8	40% H ₂ SO ₄	1,440	6,160	2,520	40,200	13,800	748	121	7,230	48,000
C9	30% H ₂ SO ₄	5,230	6,190	2,600	35,200	10,300	653	101	8,110	47,000
C10	30% H ₂ SO ₄	5,230	6,550	2,400	27,300	9,710	638	122	7,970	45,600
E3	10% H ₂ SO ₄	28,200	2,200	1,700	39,100	12,500	313	193	2,500	33,800
E4	10% H ₂ SO ₄	17,800	1,960	1,580		11,500	246	125	2,290	27,200
17-6	20% H ₂ SO ₄	1,550	3,640	1,690	32,200	12,000	321	133	4,460	46,500

TABLE 15.8

SOLUBILITY OF SEWAGE SLUDGE ASH

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
18-10	Conc. HCL	75,200	3,810	1,840	32,200	11,600	310	1,340	4,420	43,600
F7	Conc. HCL	133,000	5,600	2,070	39,600	12,600	311	1,570	4,750	58,300
A9	Conc. Acetic Acid	3,630	278	268	1,220	2,730	24	332	78	62
A10	Conc. Acetic Acid	3,970	292	248	1,230	2,720	38	325	83	50
B7	50% Citric Acid	82,900	699	598	17,200	8,920	68	456	1,510	29,300
B8	50% Citric Acid	59,800	549	461	12,100	6,610	54	429	1,120	26,200

TABLE 15.9

SOLUBILITY OF SEWAGE SLUDGE ASH

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
B1	40% NaOH		232	11	158	3	21	75	2,000	27,600
B2	40% NaOH		279	25	146	4	10	92	2,230	39,500
B5	9% H ₂ O ₂ 70% H ₂ SO ₄	47,800	6,340	394	7,030	10,600	113	272	8,250	44,000
B6	9% H ₂ O ₂ 70% H ₂ SO ₄	49,500	7,170	399	12,100	9,710	107	288	8,860	42,100
B9	1% EDTA	51,200	592	913	9,560	7,560	2,310	650	784	29,000
B10	1% EDTA	43,700	287	743	6,200	6,230	71	659	531	24,900
B11	30% Deter- gent in Water		788	172	266	276	527	269	88	

TABLE 15.10

SOLUBILITY OF SEWAGE SLUDGE ASH

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
B13	30% Na ₂ S ₂ O ₇ 70% Water	12,100	4,440	2,180	28,500	14,800	567	104	6,920	50,700
E5	20% Na ₂ S ₂ O ₇ in H ₂ SO ₄	57,300	1,360	1,330	1,190	1,530	330	286	2,810	50,500
E6	20% Na ₂ S ₂ O ₇ in H ₂ SO ₄	110,000	3,160	2,430	1,850	2,230	287	235	4,450	26,800
E7	10% Na ₂ S ₂ O ₇ in H ₂ SO ₄	81,400	282	2,590	1,240	4,350	298	237	6,450	46,000
E8	10% Na ₂ S ₂ O ₇ in H ₂ SO ₇	35,900	335	1,270	656	1,740	215	210	2,680	21,800
E9	5% Na ₂ S ₂ O ₇ in H ₂ SO ₄	56,100	481	1,600	624	2,500	282	328	7,300	43,000
E10	5% Na ₂ S ₂ O ₇ in H ₂ SO ₄	81,200	1,130	2,090	615	3,740	337	194	6,230	36,500
E11	1% Na ₂ S ₂ O ₇ in H ₂ SO ₄	72,500	523	2,370	771	5,330	350	226	7,430	41,400
E12	1% Na ₂ S ₂ O ₇ in H ₂ SO ₄	66,400	842	2,050	485	3,660	284	205	5,720	37,700
E13	20% Na ₂ S ₂ O ₇ in 50% H ₂ SO ₄	4	5,520	2,290	38,600	12,00	103	27	8,070	40,300

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
E14	20% Na ₂ S ₂ O ₇ in 50% H ₂ SO ₄	11	5,700	2,370	40,900	12,000	143	35	8,140	41,300
E15	10% Na ₂ S ₂ O ₇ in 50% H ₂ SO ₄	10	7,540	2,600	46,200	13,300	137	43	8,190	45,600
E16	10% Na ₂ S ₂ O ₇ in 50% H ₂ SO ₄	4	6,510	2,820	46,100	14,400	132	33	9,350	49,100
E17	5% Na ₂ S ₂ O ₇ in 50% H ₂ SO ₄	6	5,110	2,120	36,700	11,400	128	25	7,820	38,000
E18	5% Na ₂ S ₂ O ₇ in 50% H ₂ SO ₄	8	5,460	2,300	40,700	11,300	140	24	7,770	41,200
E19	1% Na ₂ S ₂ O ₇ in 50% H ₂ SO ₄	6	5,930	2,600	45,800	12,900	151	31	8,300	46,100
E20	1% Na ₂ S ₂ O ₇ in 50% H ₂ SO ₄	8	5,690	2,370	39,700	12,200	187	54	7,340	44,200

TABLE 15.11

SOLUBILITY OF SEWAGE SLUDGE ASH

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
F1	20% Na ₂ S ₂ O ₇ 80% H ₂ O	17,700	1,370	1,530	15,700	8,900	146	128	2,070	48,800
F2	20% Na ₂ S ₂ O ₇ 80% H ₂ O	17,600	1,550	1,500	19,500	9,800	154	129	1,980	49,000
F3	10% Na ₂ S ₂ O ₇ 90% H ₂ O	20,300	599	1,340	11,000	10,400	79	141	1,470	48,100
F4	10% Na ₂ S ₂ O ₇ 90% H ₂ O	19,300	592	1,330	11,200	10,600	85	142	1,210	47,800
F5	5% Na ₂ S ₂ O ₇ 95% H ₂ O	18,800	230	974	4,490	9,000	42	144	570	33,100
F6	5% Na ₂ S ₂ O ₇ 95% H ₂ O	17,500	256	1,060	5,300	9,440	46	105	513	34,400

TABLE 15.12

FUSION DATA

	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
NaOH fusion	74.7	7,240	31.8	40.8	6.0	106	39	81	38,600
NaOH fusion	36	8,280	27.0	37.0	6.0	101	53	102	21,200
Na ₂ S ₂ O ₇ Fusion 48,500		5,810	2,580	35,000	13,700	471	436	9,940	32,000
Na ₂ S ₂ O ₇ Fusion 40,800		7,120	2,920	42,300	15,100	630	341	11,200	41,600
Na ₂ S ₂ O ₇ Fusion 49,900		6,790	2,880	36,000	15,300	529	488	10,100	34,500
Na ₂ CO ₃ Fusion 28		6,930	4	32	12	65	0.0	0.0	17,500

All data expressed as µg/g ash

TABLE 15.13

SODIUM CARBONATE FUSION DATA

	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
Water Solubles	28	1,880	4	32	12	67	--	--	17,500
Acetic acid solubles	62,700	8,130	3,980	23,400	9,120	305	1,480	6,540	354
HCL solubles	50,200	793	1,050	25,800	6,540	226	1,340	4,360	--
TOTAL	113,000	10,800	5,030	49,200	15,700	598	2,820	10,900	27,900

Ashes were fused with Na_2CO_3 and the cold melt solubilized in water, the residue treated with acetic and hydrochloric acid in two stages. All figures given in $\mu\text{g/g}$ ash

TABEL 15.14

SODIUM CARBONATE FUSION DATA

	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
Water Solubles	43	6,930	17	26	2	171	40	47	22,500
Acetic Acid solubles	74,400	1,660	2,960	16,000	9,950	79	1,020	6,520	219
HCL solubles	37,700	862	1,170	32,100	6,160	386	1,560	4,860	30,800
	=====	=====	=====	=====	=====	=====	=====	=====	=====
TOTAL	112,000	9,450	4,140	48,100	16,100	536	2,630	11,400	53,500
	=====	=====	=====	=====	=====	=====	=====	=====	=====

Ashes were fused with Na_2CO_3 and the cold melt solubilized in water, the residue treated with acetic and hydrochloric acid in two stages. All figures given in $\mu\text{g/g}$ ash.

TABLE 15.15

SODIUM CARBONATE FUSION DATA

	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
Water solubles	4.7	6,030	30	77	--	--	--	248	5,790
Aqua regia solubles	118,000	1,580	2,140	50,300	15,800	463	1,800	11,100	42,700
TOTAL	118,000	7,600	2,170	50,400	15,800	463	1,800	11,400	48,500

Ashes were fused with Na_2CO_3 and the cold melt solubilized in water, the residue treated with aqua regia.
All figures given in $\mu\text{g/g}$ ash.

TABLE 15.16

SODIUM CARBONATE FUSION DATA

	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
Water solubles	39.6	8,820	6.3	90.0	15.6	28.1	6.3	3.6	22,800
Acetic acid solubles	108,000	138	4,500	37,100	15,600	1,171.5	1,420	15,000	24,200
HCL solubles	0.7	--	0.0	5.8	2.1	0.0	--	0.1	2.7
	108,000	8,960	4,500	37,200	15,600	1,200	1,430	15,000	47,000

Ashes were fused with Na_2CO_3 and the cold melt solubilized in water, the residue treated with acetic and hydrochloric acid in two states. All figures given in $\mu\text{g/g}$ ash.

TABLE 15.17

SODIUM CARBONATE FUSION DATA

	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
Water Solubles	38.3	8,850	6.4	90.1	15.8	27.3	6.4	3.5	23,100
Acetic Acid Solubles	107,000	140	4,610	35,200	15,700	1,097	1,480	14,700	23,700
HCL solubles	0.6	--	0.0	5.5	2.0	--	--	0.1	2.4
TOTALS	107,000	8,990	4,620	35,300	15,700	1,120	1,490	14,700	46,800

Ashes were fused with Na_2CO_3 and the cold melt solubilized in water, the residue treated with acetic and hydrochloric acid in two stages. All figures given in $\mu\text{g/g}$ ash.

TABLE 15.18

EFFICIENCY OF DIFFERENT ANALYTICAL RECOVERY SYSTEMS

	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
Perchloric acid digestion	123.9	92.1	147.1	103.9	130.9	155.9	93.2	108.6	42.8
Hydrochloric acid digestion	113.9	113.4	109.3	101.0	108.1	104.6	92.4	110.2	111.9
NaOH fusion	118.1	180.5	138.1	109.0	136.6	196.4	144.0	186.3	102.1

Basis: aqua regia solubility = 100%

TABLE 15.19

SODIUM CARBONATE FUSION DATA

	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
Water solubles	37.4	8,830	5.9	89.0	15.8	27.7	6.4	3.5	23,100
Acetic acid solubles	108,000	136	4,690	36,300	15,700	1,180	1,410	15,000	23,500
HCL solubles	0.7	--	0.0	5.8	2.1	0.0	--	0.1	2.4
TOTAL	108,000	8,970	4,700	36,400	15,700	1,200	1,420	15,000	46,600

Ashes were fused with Na_2CO_3 and the cold melt solubilized in water, the residue treated with acetic and hydrochloric acid in two stages. All figures given in $\mu\text{g/g}$ ash.

TABLE 15.21

SODIUM CARBONATE FUSION DATA

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
51B	H ₂ O	43	6,930	17	26	2	171	40	47	22,500
	CH ₃ COOH	74,400	1,660	2,960	16,000	9,950	79	1,020	6,520	219
	HCL	37,700	862	1,170	32,100	6,160	286	1,560	4,860	30,800
		_____	_____	_____	_____	_____	_____	_____	_____	_____
TOTAL		112,138	9,452	4,147	48,126	16,112	536	2,620	11,427	53,519
		=====	=====	=====	=====	=====	=====	=====	=====	=====

Ashes were fused with Na₂CO₃ and the cold melt solubilized in water, the residue treated with acetic and hydrochloric acid in two stages. All figures given in µg/g ash.

TABLE 15.20

SODIUM CARBONATE FUSION DATA

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
F9	H ₂ O	5	6,030	30	77	--	--	--	248	5,800
	AQUA REGIA	118,000	1,580	2,140	50,300	15,800	463	1,800	11,100	42,700
		-----	-----	-----	-----	-----	-----	-----	-----	-----
TOTAL		118,005	7,610	2,170	50,377	15,800	463	1,800	11,348	48,500
		=====	=====	=====	=====	=====	=====	=====	=====	=====

Ashes were fused with Na₂CO₃ and the cold melt solubilized in water, the residue treated with acetic and hydrochloric acid in two stages. All figures given in µg/g ash.

TABLE 15.22

SODIUM CARBONATE FUSION DATA

<u>SAMPLE NUMBER</u>	<u>SOLVENT</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
51A	H ₂ O	28	1,880	4	32	12	67	-	-	17,500
	CH ₃ COOH	62,700	8,130	3,980	23,400	9,120	305	1,480	6,540	354
	HCL	50,200	793	1,050	25,800	6,540	226	1,340	4,360	35,800
		_____	_____	_____	_____	_____	_____	_____	_____	_____
<u>∞</u>	TOTAL	112,928	10,803	5,034	49,232	15,672	598	2,820	10,900	53,654
		=====	=====	=====	=====	=====	=====	=====	=====	=====

Ashes were fused with Na₂CO₃ and the cold melt solubilized in water, the residue treated with acetic and hydrochloric acid in two stages. All figures given in µg/g ash.

TABLE 15.23

TYPICAL ELUTION DATA, CATION EXCHANGE COLUMN

<u>FRACTIONS</u>	<u>Ca</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Mg</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>	<u>P</u>
#1	17,600	18	0.6	0.6	2,280	85	50	1.0	12
#2	47,500	100	1.0	7.0	6,390	233	285	--	1,460
#3	42,300	112	5	3	5,320	188	353	0.6	3,830
#4	7,850	49	10	4	973	33	180	0.6	4,020
#5	2,520	43	23	8	304	31	100	1.0	4,290
#6	191	28	33	5	138	18	44	1.0	3,440

All data expressed as $\mu\text{g/g}$ ash.